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# LIBS 2000



## Book of Abstracts

**First International Conference on Laser Induced  
Plasma Spectroscopy and Applications  
Tirrenia, 8-12 October 2000**

# LIBS 2000

*1<sup>st</sup> International Conference on Laser Induced  
Plasma Spectroscopy and Applications  
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## **Laser-Induced Breakdown Spectroscopy: The Past and Future**

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Since the first laser plasma was generated in the early 1960's until the early 1990's, with a few exceptions, interest in the laser spark has been directed mainly toward fundamental studies of its characteristics under different conditions. That is, it was basically a scientific curiosity. From a broad perspective, however, LIBS has the potential to be the most versatile method of elemental analysis because of its many unique capabilities. These capabilities include the ability to conduct non-invasive, in situ measurements, the absence of sample preparation, near real-time analysis, and good sensitivity for many elements. Many strengths of the LIBS approach meet analysis requirements that cannot be met by conventional analytical methods. With the development of robust and compact laser systems and associated instrumentation including spectrometers and detectors, there has been significant increased interest in the technique for practical applications. This interest has been driven by practical concerns for environmental monitoring and the need for real-time process monitoring for industry and mining. LIBS investigators are presently addressing some of these needs while other needs await future development. Esoteric applications such as art conservation and space exploration are also being considered. Recently, a few LIBS-based instruments have become commercially available. Many of these potential applications, however, will require research into the factors affecting the quality of LIBS-based analyses as many of the inherent advantages of the technique also limit its analytical usefulness. Methods are needed to increase measurement accuracy and precision and to minimize or correct for physical and chemical matrix effects. An overview of the history of LIBS will be presented here together with a vision for the future of the technique.

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## **Analysis of Environmental Pb Contamination: Comparison of LIBS Field and Laboratory Instruments**

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The U.S. Army Research Laboratory has been active in LIBS research for over a decade. The early work was focussed on the use of uv pulsed (excimer) lasers for the production of sparks in gas flows (Morris, 1990) while more recently we have developed LIBS for the detection of halon replacement compounds and refrigerants (Lancaster, 1999). In the past few years we have seen a significant growth in the number of LIBS applications of interest to the military. Application areas include detection of toxic metals in soils, waters, and airborne particulate matter as well as the detection of hazardous chemicals such as explosives and chem/bio agents. Part of our effort in developing LIBS sensor technology involves collaboration with industry towards the commercialization of this technology. This is being done through the Small Business Innovation Research (SBIR) program.

During the initial stage of the SBIR program project, a field-portable LIBS instrument was developed by ADA Technologies, Inc. and the concept of detecting Pb in paint and soil was validated under laboratory conditions through the analysis of samples with differing Pb contents. During the second stage of the project, the portable LIBS instrument was upgraded and field tested in Panama, Colorado, and California for the detection of Pb in paint flakes and on painted surfaces. The LIBS instrument also was able to detect Pb collected on PM-10 air filters from local air monitoring stations in Panama City, Panama as well as Pb in contaminated soils from sites at Fort Carson, Colorado and Sierra Army Depot in California. The field instrument uses a passively Q-switched Nd:YAG laser as well as an ungated photodiode array detector. Differences in performance between the field unit and our laboratory system will be discussed.



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## LIBS Applications for Production Control in Steel Industries

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Recent progress in sensitivity connected with an advanced design of equipment enable the laser-induced breakdown spectrometry (LIBS) to meet the requirements of real-world applications. Elemental analysis for production control in steel industry is one example. In this contribution, the state of the art is summarized and applications such as the identification of steel products, the analysis of liquid steel and the fast determination of steel cleanness are described.

For the final inspection of the steel grade of pipe fittings, two machines based on LIBS were developed and installed in a production line. The steel grade is of decisive importance if the pipe fittings are exposed to corrosive fluids, e.g. in the oil and chemical industry. In order to avoid a leakage due to corrosion with considerable consequential costs and possibly catastrophic environmental damage, one has to assure that always the proper steel grade is applied and no accidental mix-up occurs. According to product liability the producer of pipe fittings is interested to perform a 100% inspection of his products. The machines installed in Germany and Malaysia control each pipe fitting automatically within 2 seconds. An expert system was developed for the classification of up to 30 steel grades from the measured data. More than 400 000 pipe fittings were inspected during the last 18 months, and the experience on the routine operation of the machines is reported.

Increasing standards for steel qualities require advanced methods of steel analysis, especially during secondary metallurgy in steel works. The fast multi-elemental laser analysis of liquid steel has the potential to replace the spot checks of today by a more representative measurement. Preconditions are the sufficient analytical performance, i.e. limits of detection (LOD) of less than 10 µg/g for most of the relevant elements, and the reliable optical access to the steel melt. By using a sensitivity-enhanced LIBS design we measured LOD values in the vicinity of 10 µg/g and below for the crucial elements C, P, S as well as for other elements such as Cr, Ni, Mn and Si. Furthermore, we report about operational tests of an immersion lance which permits the optical access to the melt for the laser analysis. Operational periods of more than 4 hours with the lance immersed into a 100-kg steel melt at a temperature of about 1630°C and running laser analysis were demonstrated successfully with this equipment.

The rapid determination of steel cleanness is important in the production of high-quality steel for springs, thin foils and wires, because inclusions of e.g. Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> with typical grain sizes of 0.1 – 100 µm have a deleterious effect on the physical properties of steel. For product development, process control and quality assurance, a fast method is required to identify and quantify such inclusions. For this application, a scanning LIBS apparatus was developed consisting of a diode-pumped laser, a Paschen-Runge vacuum spectrometer, a fast multi-channel integrating electronics, translation stages and an automatic control for most operations. The laser allows repetition rates of up to 1 kHz and, due to its good beam quality, small focal spot sizes are possible resulting in a spatial resolution of 20 µm.

In summary, it is demonstrated that LIBS is a versatile tool for steel analysis in production control and the technique is no longer restricted to laboratory use only.

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## **Laser Induced Breakdown Spectroscopy: a New Analytical Tool in Art Conservation and Archaeology**

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An overview of the use of Laser Induced Breakdown Spectroscopy (LIBS) as an analytical tool in the fields of art conservation and archaeology is given with emphasis on the identification of pigments in painted works of art and the analysis of materials in archaeological findings. Several examples, which demonstrate the application of LIBS in different cases, are presented including pigment analysis in easel and wall paintings, icons, illuminated manuscripts and ceramic sherds (Anglos 1997; 1999). The optimization of critical experimental parameters for the successful application of LIBS in the examination of artworks is discussed in relation to the sensitivity, value and aesthetic content of such objects. In this respect the applicability in situ and the nearly non-destructive character of LIBS are key features especially in view of the strict limitations imposed on sampling objects of art. Finally future trends regarding the use of LIBS in combination with other spectroscopic techniques such as Raman microscopy (Burgio 2000) and Laser Induced Fluorescence (LIF) spectroscopy are also discussed.

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## **Laser-Induced Fluorescence Probing During Pulsed-Laser Ablation For Three-Dimensional Number Density Mapping of Plasma Species.**

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One of the major drawbacks of thin film deposition by pulsed-laser ablation is the lack of understanding of the fundamental mechanism involved into the deposition process. In particular, the role of gas-phase reactions during reactive laser ablation and the plasma-substrate interaction are critical steps which need a deeper insight. In this framework, density measurements of the species ablated from the target surface and those formed in the gas-phase have been performed using laser-induced fluorescence (LIF) probing during titanium and aluminium ablation in low-pressure atmospheres of either oxygen or nitrogen. LIF measurements allow the probing of ground-state atomic or molecular species which make this technique particularly interesting for detection of species in the vicinity of the substrate which is placed at a distance of several centimetres from the irradiated target. In this region, the plasma temperature is low and most atoms or molecules are in the fundamental electronic state. In the present study, a beam expander was used to transform the dye laser probe beam in a thin plane section of  $0.1 \times 40 \text{ mm}^2$  dimension. The LIF signal was recorded using a fast intensified charged coupled device of  $576 \times 384$  pixel. In this configuration, three-dimensional number density mapping of ground-state species was possible. From the variation of the time delay between the ablating laser and the probe laser pulse, a detailed picture of the time- and space evolution of the probed species was acquired. The LIF measurements are complementary to emission spectroscopic measurements which have been used to detect excited species in the plasma region of higher temperature.



## LIBS for Qualitative Correlation Analysis of Inorganic Solids, Plastics, and Particulate Materials

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Realizing the great importance of LIBS for quantitative spectrochemical analysis, we note that not much attention has been paid until now to the potential of LIBS for rapid, reliable qualitative analysis. In this sense we do not seek a detailed chemical composition but rather that the material be instantly identified using its unique spectral "fingerprint." This "fingerprint" is a LIBS-spectrum chosen from LIB spectra of a variety of compounds by a robust correlation procedure. This implies that corresponding data bases exist which contain LIB spectra of a variety of compounds, such as exist for IR, X-ray, or mass- spectrometry. The necessity of using such LIBS libraries, in addition to well-known tables of spectral lines, stems, first, from the specifics of LIBS emission spectra, which are usually dominated by ionic lines, and, second, from their complex matrix-dependence which often inhibits the direct relation between a sample content and the intensities of spectral lines.

We developed a compact laser induced breakdown spectrometer with microscopic sample imaging for instant classification of solid, particulate, and organic materials. Two thousand data points (pixels) represented a sample spectrum for which we found that the use of simple linear and non parametric (rank) correlations to be entirely satisfactory for spectra identification. Software was developed which combined both data acquisition and data treatment functions.

The robustness of the technique was demonstrated by the nearly 100 % reliable identification of compositionally similar (a) solids (Gornushkin, 1999): stainless steel and cast iron standards, (b) particulate (Gornushkin, 2000) : NIST and natural iron ore samples, and, (c) plastics (Anzano, 2000): polyethylene, polyvinyl chloride, polypropylene, etc. In the case of iron ores, chemical speciation of iron compounds was also demonstrated.

The attractive features of the technique are its simplicity, small size, low cost and a good potential for identification of various kinds of materials without preliminary sample preparation. In the current design, based on a miniature fiber optic spectrometer, the technique has one limitation: its sensitivity is quite low and therefore spectral information from minor components (0.1-1 %) is lost. However, this drawback can easily be overcome by using more sensitive detectors, like intensified CCD's. Overall, we demonstrated that the technique can have immediate application for on-line, real-time analysis of raw materials which is important in the mining and chemical processing industries. Potentially, it can also be applied in forensic, environmental, medical and other fields.

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## **Resonance-Enhanced Laser-Induced Plasma Spectroscopy for Elemental Analysis**

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A novel analytical technique based on resonance-enhanced laser-induced plasma spectroscopy was demonstrated. It has the advantages of laser-induced breakdown spectroscopy, yet without the problems associated with hot plasmas such as intense continuum emissions. This was possible because the electrons needed to impact-excite the analytes were generated nonthermally by resonant photoionization of the host species in the plume. The very encouraging results of pilot studies will be reported.

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## Plasma Imaging for Improved LIBS Analysis

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We report the development of plasma imaging setups and their evaluation for improvement of LIBS analytical results. An imaging setup based on Fourier transform spectroscopy provided detailed maps of the plasma, with full spectral information in each pixel. Preferred locations in the plasma, optimized for the analysis of some elements, were found. The imaging data was also applied for optimization of the optical setup and for understanding the effects of the focusing and energy flux conditions.

Another imaging setup was applied for single-shot plasma and provided a combination of spectral and spatial resolution. It consisted of a new multifiber imaging spectrometer, coupled with an ICCD detection system. This optically interfaced setup was used for optimization of the LIBS parameters and for compensation for matrix effects. An investigation of matrix effects in analysis of Pb in natural soils was carried out using this setup. A clear global optimum was observed for analyte signal as a function of location and time, indicating the best experimental conditions. The spatial distribution of the internal plasma temperature, and the related matrix effects were also studied.

On the basis of the above spatial resolution of LIBS signals, we suggested a new low-cost setup that may replace the expensive gated detectors, while maintaining acceptable analytical figures. The proposed setup was a result of investigation of plasma-front propagation in LIBS analysis. A proper observation geometry, perpendicular to the plasma expansion vector, enabled conversion of spatial to temporal resolution. A multifiber imaging spectrometer provided information corresponding to a series of delay times, which was found adequate for analysis of a variety of matrixes. The performance of the nongated detector, in terms of signal-to-background ratio, was similar to that of a gated one.

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## **Influence of the Optical Density on Spectral Line Emission from Laser-Induced Plasmas**

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Laser-induced plasmas (LIP) are emission sources that generally present a high density of atoms and ions. As a consequence, the emission of spectral lines is often characterised by a high optical density, due to the autoabsorption of the emitted radiation within the LIP. The optical density and the subsequent saturation of the line intensities are determined by two main factors in a given experiment. On one side, for a certain emission line, the saturation depends on the density of atoms present in the LIP, which is related to the concentration of the particular element in the sample. In the analytical applications (LIBS) this saturation is reflected in the calibration curves, which are linear only for low concentrations, and bend in the high-concentration region, as has been found in several works (Leis *et al.* 1989, Sabsabi *et al.* 1995, Aragón *et al.*, 1999). On the other side, the optical density depends on atomic parameters of the particular spectral line. The curve of growth methodology, which allows to relate the emission intensities to the optical density has been applied in a recent work (Gornushkin *et al.*, 1999) to LIP emission spectroscopy.

In the present work, we have investigated the iron line emission from a LIP generated with iron-nickel alloys for varying values of optical density. The plasmas have been generated using a Nd:YAG laser in air at atmospheric pressure. In order to extend the range of optical densities, the samples used include a wide range of iron concentrations (0.2–95.0 %). Also, the emission intensity is measured for Fe I lines with different values of the oscillator strength. The curve-of-growth methodology is used to calculate the relative emission intensity as a function of the optical density. To this aim a simplified model of the LIP is used, in which a uniform temperature value, obtained using the Boltzmann plot method, is introduced.

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## Comparison of Femtosecond and Nanosecond Laser Induced Plasma Emission

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Wide range of LIBS applications encourages further attempts for its improvement. Lots of effort has been put in the better understanding of the laser ablation plasma dynamics. One of the major obstacles so far has been the fact that the plasma is ignited during the laser pulse itself. The time scale of material removal is of the order of 100 ps (mainly depending on the properties of the material ablated) which is smaller than the pulse lengths of the most commonly used nanosecond lasers. The plasma absorbs a part of the laser radiation making the amount of the laser energy coupled to the sample smaller and hard to define. Since plasma density depends on the efficiency of the material removal and the amount of material removed on the energy coupled to the sample, it is extremely difficult to predict plasma parameters for the ablation with lasers of such pulse lengths.

Laser ablation process with femtosecond lasers is simpler in a sense that the process of energy transfer to the sample is completed before the onset of the material removal from the surface. Typical laser intensities are of the order of  $\text{TW}/\text{cm}^2$ . The sample is heated to the temperature close to the critical temperature and the mechanism responsible for material removal is phase explosion.

The aim of this experiment was to compare plasma conditions during ablation with fs and ns laser of same wavelength and energy by means of the time resolved optical emission spectroscopy. 160 fs and 6 ns laser pulses ( $\lambda=775 \text{ nm}$ ,  $E<500 \text{ }\mu\text{J}$ ) were used for ablation of copper and brass samples in an argon atmosphere. Optical emission from the ablation plasma was studied in a side-view arrangement. Differences in the temporal development of atomic and ionic line intensities, as well as the spatial plasma emission profiles and pressure dependence of line intensities for the fs and ns laser ablation stem from different plasma starting conditions and lack of the plasma shielding in the fs case. From these studies optimal conditions for the analytical application of LA-OES (LIBS) were chosen.

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## **Échelle Spectrometer for Materials Analysis by Laser Induced Plasma Spectroscopy**

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Most of the Laser Induced Plasma Spectroscopy (LIPS) work published in the literature has been carried out by using a conventional Czerny-Turner spectrometer coupled with a detector [intensified charge coupled device (ICCD), CCD, intensified photodiode array (IPDA), or photomultipliers] and very few by using an échelle spectrometer. Linear photodiode arrays or ICCD, when they are attached to a conventional Czerny-Turner spectrometer, only allow a limited spectral coverage (typically a few nm wide) while an échelle spectrometer provides a wide range of spectral wavelength. Recently, we have seen the arrival of a new commercial optical detector system coupling échelle spectrometer with time-gated ICCD detector, which enables simultaneous measurements of spectral lines in a wide range with enhanced resolution. To our knowledge, no evaluation of a commercial system based on an échelle/ICCD combination for Laser Induced Plasma Spectroscopy (LIPS) has been published.

In this work we evaluate the performance of a commercial échelle spectrometer coupled with an ICCD detector for the analysis of solid samples by LIPS in air at atmospheric pressure. We compare results obtained in aluminum alloy samples with this system and with a "conventional" Czerny-Turner spectrometer coupled to an IPDA in terms of analytical precision and limit of detection of minor and trace elements. Our results indicate that no significant differences in terms of analytical figures of merit exist between the échelle/ICCD system and a conventional system based on 0.67 m Czerny-Turner spectrometer with IPDA.

The second part of this work aims to present a critical view of the échelle spectrometer for LIPS applications in terms of advantages and limitations. The limitations can be inherent to the dispersion method or resulting from the dynamic range of the detector. For example "blooming" phenomena occur entailing the appearance of ghost emission lines. On the other hand, the échelle spectrometer allows complete elemental analysis in single shots as spectral lines of major, minor and trace constituents, as well as plasma parameters, are measured simultaneously. This enables a real time identification of unknown matrices and an improvement of the analytical precision by selecting several lines for the same element. The échelle spectrometer also allowed to check the validity of the local thermodynamic equilibrium (LTE) conditions in LIP, since the electron density and the plasma temperature were determined simultaneously for single shots by several methods. Plasma temperature was determined by a Boltzmann diagram using several iron lines and the electron density by Stark broadening of Al II, Si I and Mg I lines. We also determined the ionization temperature by using Saha's law. A discussion of the LTE conditions in LIP will be presented.

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## CF-LIBS: A New Approach to Quantitative LIBS Analysis

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In last years, the LIBS (Laser Induced Breakdown Spectroscopy) technique, also known as LIPS (Laser Induced Plasma Spectroscopy), LAS (Laser Ablation Spectroscopy), LSS (Laser Spark Spectroscopy) or LAOES (Laser Ablation Optical Emission Spectroscopy) has become a viable method for fast qualitative or semi-quantitative analysis of material. A number of applications have been proposed in many different fields, ranging from Cultural Heritage studies, Industrial Processes control, Bio-medical applications, etc.

The possibility of obtaining in a very short time, without treatment of the sample, useful information about its elemental composition, has pushed many researchers towards the development of new analytical tools for making LIBS quantitative. The toughest difficulty to overcome, in order to obtain quantitative results with the LIBS technique, is the so-called 'matrix effect', i.e. the strong dependency of LIBS spectra on even slight variations of the composition of the matrix in which the elements of interest are embedded.

The usual approach to LIBS measurements, based on the use of calibration curves or reference samples, cannot be used on *a priori* unknown samples. Moreover, measurements on the reference samples must be taken in exactly the same experimental conditions used for the actual measurements; every variation in laser energy or laser-sample coupling turns on additional experimental errors in the elemental concentration determination.

In 1997, the authors proposed and patented a new method for standard-less LIBS analysis, called Calibration-Free LIBS (CF-LIBS). The Calibration-Free LIBS method overcomes the matrix effect, giving a precise quantitative elemental analysis of the sample without using any kind of calibration curve or reference sample. With the CF-LIBS technique all the plasma parameters are measured from the plasma, so that the use of CF-LIBS allows to automatically compensating for laser power fluctuations and variations in the laser-sample coupling. This feature might reveal essential in practical applications, and in particular in hostile environment (vibrations, heat, etc...). Moreover, CF-LIBS is a blind technique, i.e. it can be used on *a priori* unknown samples with errors of the order of the concentration of elements not identified – and in general almost all the elements have measurable lines in the near UV-Visible spectral range.

In this presentation, a discussion will be also given about non-ideality of plasma conditions, and the possible improvements of the CF-LIBS algorithm.



## Analysis of Bacteria by Time Resolved Laser Induced Breakdown Spectroscopy

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Time REsolved Laser Induced Breakdown Spectroscopy method (TRELIBS) has been developed at the Centre d'Etudes du Bouchet (CEB), to answer the real necessity of rapidity, sensitivity and selectivity in detection of gases or polluted surfaces. Focusing a powerful laser pulse on a surface produces the vaporization of a small amount of the sample materials, then induces, near the focal region of the lens, a high temperature plasma. By using spectrally time resolved plasma emissions, the elemental composition of the material can be determined.

Our goal is to design a miniaturized system for the in-situ analysis in military and civilian applications, with a real time detection and identification for biological and chemical agents.

After several studies in the chemical domain, we now want to adapt this technique of analysis in the framework of the detection and the identification of bacterial pollutants. To do that, we used bacteria with chemical composition and geometrical properties very well known (e.g. *Bacillus subtilis globigii*).

Therefore we carried out a mapping of different cationic ratios. Indeed the cationic ratios that characterize a bacterial strain allow to qualify it on any substrates (bacterial carpet on nutritive environment (agar), freeze-dried bacteria, bacterial aerosols or bacteria in water suspension). Moreover, the presence of atomic signals specific to a bacterial strain (Li for example) must lead to an identification process.

The first analysis on *Bacillus globigii* on agar as nutritional environment have allowed us to determine the most intense emission lines for different characteristic elements of bacteria. Thus, three lines from magnesium are identifiable: two ionic lines at 279.553 nm and 280.270 nm, and more an atomic line at 285.213 nm. Another spectral window allows the identification of the two ionic lines of calcium to 393.366 nm and 396.847 nm. The double lines of sodium are easily identifiable at 588.995 nm and 589.592 nm. Finally, two atomic lines of potassium are found at 766.490 nm and 769.896 nm. Other known elements can be qualified: P, S as for chemical warfares but also Fe, Mn, Zn, Cu, Co, Mo...

Next we are focusing on the evolution of the emission lines intensities according to the number of laser shots at the same location. So, we can see that the very first shots distinguish the bacteria from its nutritive environment and, little by little, after several pulses, the atomic line intensities for the bacterium and the agar look the same.

This study has shown the possibility of qualification of bacteria by the TRELIBS method and the necessity to extend the analysis to other substrates for bacteria. The main objective in next steps for biological detection is to create a data bank on cationic ratios for different bacteria with other bacillus such as *Bacillus thuringensis*, and to try with another types of bacteria such as *Staphylococcus*, *Proteus mirabilis*, or *Escherichia coli*.

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## LIBS on Human Teeth and Dental Materials

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Here we report on the application of Laser Induced Breakdown Spectroscopy (LIBS) to the analysis of important minerals and potentially toxic elements within teeth. We have carried out a series of experiments to trace the influence of environmental factors on the accumulation of a number of elements in teeth. Common exposure of teeth to numerous chemical compounds is encountered when eating, when brushing teeth for cleaning, or when undergoing dental treatment.

In this study, we investigated a range of different types of samples, including

- Teeth (first teeth of infants, and second teeth of children, adults). Two different methods were used to investigate the samples. Firstly, simple depth profiling of tooth was attempted. Secondly, the samples were cut into slices of about 1.5 mm thickness and subsequently the cross-sections of teeth were investigated.
- Dental amalgam (low-copper alloy – Ag, Sn, Cu and Zn).
- Composite restorative material (containing glass filler particles with Zr, Al and Cr as major constituents)
- Tooth pastes with and without whitening additives – alumina ( $\text{Al}_2\text{O}_3$ ) and anatase ( $\text{TiO}_2$ ).

Trace elemental profiling in teeth, using LIBS, provide vital information for environmental monitoring [Samek et al. (1999)]. For teeth where a time axis exists within a sample, the time/concentration relation can be monitored. This information is destroyed by the dissolution approach in different techniques on basis of atomic absorption spectroscopy which are currently used [see e.g. Spevackova and Smid (1999)]. Here we present 2D maps of elemental distribution in teeth for different elements, thus the time/concentration relation can be linked to environmental exposure. Comparison of element distribution in teeth from different countries is also given. Maps of migration of the elements, which are presented in different teeth fillings, to the tooth matrix are also presented. Finally, caries can be identified through decrease in mineralising elements Ca and P concentrations while non-mineralising elements and organic material increase.

In order to obtain quantitative results the two methods have been used in our study (note, that there are no solid reference samples available for human teeth). Firstly, reference samples in the form of pellets with tooth-equivalent material have been pressed for constructing standard calibration curves. Secondly, a similar approach of the calibration free method to that proposed by Ciucci et al. (1999) was used.

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## **Analysis of Pharmaceutical Materials by Laser-Induced-Plasma Spectroscopy (LIBS)**

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### **Purpose**

Laser-Induced Breakdown Spectroscopy (LIBS) is being developed as a new analytical tool for the rapid determination of drugs and pharmaceutical materials in intact solid dosage forms.

### **Methods**

The LIBS system consists of a Nd:YAG laser (1064 nm) which is focused on tablet samples positioned on a X-Y-rotating stage to ablate material and generate a plasma. Light emitted from the plasma is transferred via a fiber optic bundle to a spectrometer equipped with a gated non-intensified CCD detector. Atomic emission line intensities for target elements (F, S, Cl, Na, Mg, P) commonly found in the chemical structure of pharmaceutical materials are used for the quantitation of the drug compounds in tablets without requiring any prior sample preparation. All of the instrumentation and analysis are fully automated and controlled by an operating software allowing unattended operation for up to 26 samples. These studies are aimed at 1) characterizing the emission spectra of commonly used pharmaceutical excipients over large spectral domains and at identifying analyte emission lines for target elements such as Cl, F, S, Na, Mg and P which are present in the chemical structure of many pharmaceutical compounds; and 2) evaluating the analytical performance of a prototype instrument with respect to operating parameters, sampling strategy and formulation using model drug tablets. Tablet samples were prepared by blending excipients and model drug formulations which were compacted on an hydraulic press using round, 12.5 mm diameter tooling. The tablets were then positioned on the sample tray and analyzed by LIBS.

### **Results**

The excipients have emission spectra that are identical in spectral content, but differ slightly in the intensity of the background and emission lines and bands. The spectra have few lines and bands particularly in the UV and NIR spectral regions and therefore should minimize potential spectral interferences with analyte lines. For each target probe, interference free emission lines of sufficient intensity have been identified. Precision values of  $\leq 2\text{-}3\%$  can be achieved with analysis time of less than one (1) minute per tablet. Emission intensity is sensitive to sample geometry, particle size and sample processing method. However, when these factors are controlled, the technique provides accurate analysis when compared to an UV absorption method.

### **Conclusions**

The rapid analysis time by LIBS ( $< 1$  min per tablet), the good precision and the elimination of sample preparation make the technology potentially useful for many pharmaceutical R&D and process monitoring applications where mapping of a specific component or rapid availability of data is desirable. Accuracy is satisfactory when calibration standards are matched to the test samples.

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## **LIBSGRAIN: A European Collaborative Programme to Develop On-line Material Analysis**

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The plant in many process and utility industries operates under extreme conditions of temperature pressure and stress. The conditions are dictated by the requirement to improve the efficiency of thermodynamic cycles, improve yields or cater for new materials and processes. At the same time that the plant is operating in a more arduous regime, the capital cost and cost of downtime, particularly unscheduled downtime is rising and imposing increasing financial burdens on the operators. To maximise utilisation of the plant residual life needs to be monitored and various strategies have been adopted for this purpose. For example, welded joints are vulnerable to metallurgical changes weakening the structure. An on-line method of monitoring these changes, particularly if they can be related to residual life would be a valuable tool.

The LIBSGRAIN project was set up in order to advance the techniques of laser induced breakdown spectroscopy and develop the necessary equipment and control systems to allow it to be used on-line in very demanding applications.

Conventional metallurgical analysis of material taken from one specific plant that has been operating under condition where material species migrate and create changes in localised composition is being used to define the spatial and compositional resolution in the changes that are occurring as well as the way and rate at which these changes take place. It has been believed that very fine spatial resolution is required and a principle activity has been to create a system which can reliably achieve this resolution and which will operate under the temperature conditions necessary. A high spatial resolution implies that enormous amounts of data need to be processed if any significant area of material is to be surveyed even when areas most at risk are targeted. This problem has been approached in several ways. The analysis of individual samples has made use of calibration free techniques developed by IFAM. At the same time the actual data transfer and processing has been subject to intensive development to produce a simpler faster and easier to use system without the need for expert intervention, whilst still maintaining the analysis accuracy. In parallel with these developments, a study has been carried out into the use of statistical techniques which could allow the amount of data that needs to be processed to be reduced. Thus the confidence in the prediction of loss of residual life or the confidence in the plant integrity may be assessed from the results obtained. The ultimate objective of the analysis software and system is to achieve an intelligent expert system which could have predictive capabilities in respect of potential plant problems.

The instrumentation system that is under development has the key requirement that it should be capable of being operated on-line on plant that is operating at high (650 C) temperature. Inevitably the target area will be subject to vibration and in some process plant, for example in the petro-chemical industry there may be additional constraints due to explosion hazards than those that are normally associated with the use of high power lasers. The approach to these problems is to make use of a scanning system with feed back that is capable of compensating for the vibrational movement of the surface of the scanned material. Within this task there is more than one potentially useful approach depending on the severity of the problem. The scanning head for the system will be operating close to the high temperature surface and the detailed design includes cooling which maintains a uniform temperature both for component integrity purposes and to minimise beam distortion. The use of inert gas as a cooling medium allows operation to take place in hazardous areas.

Once the individual components of the system are operating satisfactorily, the assembled prototype will be tested on operating plant to allow evaluation and enhancements to be implemented. It is anticipated that the developed instrumentation system will be a valuable tool in the struggle against lost downtime and previously unforeseen problems.

## **Fast Analysis of Wood Preservers using LIBS**

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LIBS is used for investigations of wood preservers in timber and in furniture. Both, experiments in laboratory and practical applications in recycling facilities and on a building site prove the new possibilities for the fast detection of harmful agents in wood.

The further use resp. the recycling of contaminated wood require the analytical evaluation of the material with regard to contained toxic substances. At present, wood preservers are investigated using conventional analytical methods, which require expensive sample preparation and are difficult to use in practise. Inorganic substances are detected by atomic emission spectroscopy (ICP-AES), organic compounds are investigated using different chromatographic methods.

LIBS is the method of choice for fast on the spot analysis of harmful active agents.

It enables the user to detect main and trace elements in wood within a few seconds independent of the matrix, knowing that different kinds of wood show the same elemental composition. Sample preparation is not required.

The quantitative analysis of inorganic wood preservers (containing e.g. Cu, Cr, B, As, Pb, Hg) has exactly been performed. Statistical data were obtained from field measurements in a recycling facility. The use of correction factors, due to different penetration depths in different matrices, led to good agreement between LIBS and ICP-AES results, so that legal requirements are fulfilled. Organic wood preservers were detected only indirectly with regard to their characteristic functional groups, a rough classification was possible. LIBS-screening of the surface characterized the total grade of contamination.

A commercial system was developed for mobile Laser-Plasma-Analysis as well as for industrial use in sorting plants. The universal measuring principle in combination with an Echelle optics permits real simultaneous multi-element-analysis in the range of 200 nm - 780 nm with a resolution of a few pm. Therefore, the method offers a wide range of further applications, e.g. online analysis of food or identification of additives in plastic material.

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## On-line Monitoring of heavy Metals in Aerosols: from Laboratory Studies to industrial Applications

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Particulate heavy metals can cause severe toxic and carcinogenic effects when inhaled in higher concentrations. Therefore, it is desirable to establish a versatile instrumentation for a complete and rapid monitoring of particulate emission (e.g. waste incineration) in order to estimate hazard levels, to evaluate control systems, or to provide feedback. Due to the small mass involved, the determination of the elemental chemical composition is currently most often achieved by filter sampling, digestion, and a subsequent analysis with conventional spectroscopic methods. These techniques are time consuming and most of them do not qualify for construction of robust, mobile sensor systems with no or little required infrastructure.

The first aim of this work was to develop a transportable, low cost system for a direct analysis of aerosol filter samples based on Laser-induced Plasma Spectroscopy (LIPS), which provides quasi-on-line information on the elemental chemical composition. The system consists of a 19"-rack with a laser unit and a spectrometer/detector unit connected to a miniaturized sensor-head via fibre optics allowing a maximum flexibility of the set-up. A plasma is created by focusing the beam of a Nd:YAG-laser on the surface of a quartz-fibre filter. The filter is placed on a filter holder which can be rotated by a stepping motor for getting spectra from different locations of the filter. Only minor dependence of the LIPS-signal on the matrix was observed and the dynamic range was found to be more than three orders of magnitude. Total reflection x-ray fluorescence (TXRF) was established as an independent reference analysis for calibration of the method. Detection limits for heavy metals range from about 50 ng cm<sup>-2</sup> to about 500 ng cm<sup>-2</sup> and measurements done on filters taken in incineration plants fit well into calibration curves established with filters loaded with laboratory-generated aerosols. Besides these analytical merits of the technique we will also address the merits from a first measurement campaign at a waste incineration plant, where an automatic isokinetic filter sampling interface for particulate emission was employed.

In a second project we examined the potential of LIPS for on-line monitoring of heavy metals, i.e., Chromium at an electroplating plant. During this campaign we could demonstrate that LIPS allows the direct detection of aerosols in the exhaust stream with detection limits of 13.6 µg m<sup>-3</sup>. The latter are nearly two orders of magnitude lower than the current German threshold values for Cr (TA Luft, 1 mg m<sup>-3</sup>) and were established with measurement times of 20 seconds.

# Carbon Content Detection in High Temperature and High Pressure Fields using Laser Induced Breakdown Spectroscopy

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## 1. INTRODUCTION

Carbon content is an important factor in the operation of pulverized coal thermal power plants, and associated monitoring and control techniques are needed for continued operational improvement. LIBS is suitable for particle composition measurement because of its strong signal intensity and simplicity of apparatus<sup>(1),(2)</sup>. In this study a LIBS technique was applied to detect carbon content in pulverized coal, char, and fly ash under the high pressure and high temperature conditions that characterize PFBC and IGCC thermal power plants.

## 2. EXPERIMENTAL APPARATUS

Figure 1 illustrates the experimental apparatus. The furnace used can produce conditions in the 300K-1000K temperature and 0.1MPa-3MPa pressure ranges. The pulverized coal, char, and fly ash were added to high temperature and pressure gases, and carbon content detectability was tested in various gas compositions appearing in actual plants.

## 3. RESULTS

Figure 2 shows the comparison of the unburned carbon in pulverized coal, char, and fly ash under  $T=720K$  and  $P=3.0MPa$  conditions. The unburned carbon value was determined using LIBS signals from C, Si, Al, Fe, and Ca using a plasma temperature correction. The results show good agreement to those obtained by the conventional method. The detectability of carbon content declines at high pressure due to rapid quenching of plasma. C-based gases such as CO and CO<sub>2</sub> induce noise signals, and careful attention is needed under actual application conditions.

## 4. CONCLUSION

LIBS was applied to carbon content measurement in pulverized coal, char, and fly ash, and its applicability was tested under several gas conditions. Improved characteristics were demonstrated in terms of on-line capability and sensitivity compared to the conventional sampling method. LIBS features detection time capability of under 1 minute, as compared to over 30 minutes of sampling and analysis time required by the conventional method. LIBS therefore offers various merits as a tool for actual plant monitoring.

## ACKNOWLEDGEMENTS

This report is based on the activities of the AST (Advanced Sensing System for Thermal Power Plants) committee that has been organized by JAPEIC (Japan Power Engineering and Inspection Corporation) under the auspices of MITI (Ministry of International Trade and Industry). The authors would like to express their sincere thanks to the AST committee members, and in particular to Professor Masayuki Horio of Tokyo University of Agriculture & Technology, committee chair, and Professor Hiroshi Moritomi of Gifu University, sub-committee vice-chief, for their excellent advice.

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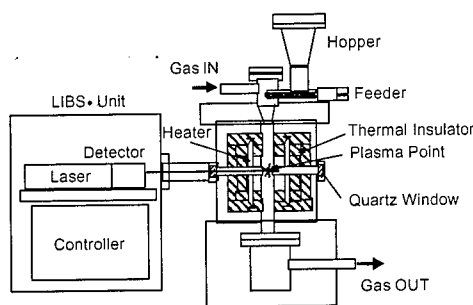


Figure 1 Experimental Apparatus

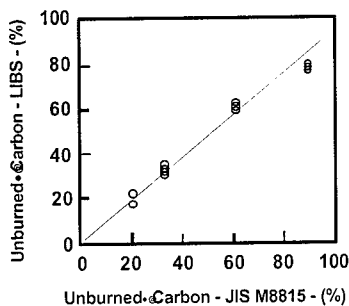


Figure 2 Unburned Carbon Measurement  
( $T=720K$ ,  $P=3.0MPa$ )

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## Femtosecond Laser Nano-Machining and the Production of Nano-scale Particles

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A unique femtosecond laser nano-machining facility has been established at the University of Nebraska. Since femtosecond lasers produce their own source of free electrons when focused to high intensities on the surface of a material, the damage thresholds are very sharp and tend to be single valued as compared to the longer pulsed nano-second lasers. Since the damage thresholds are well defined, it is possible to defeat the defraction limit of optics and thus perform unique nano-machining of materials. When the femtosecond laser is focused on a transparent surface, it is possible to produce subsurface defects of approximately 50 nm in size. These subsurface defects offer the possibility to produce permanent 3-D data storage at 10  $\mu\text{m}$  intervals below the surface of the dielectric material. In addition the femtosecond laser system can be used to drill approximately 1  $\mu\text{m}$  holes with aspect ratios greater than 30. At intensity values above the threshold it is possible to produce ablation of the surface and produce particle densities approaching the solid densities of the material being ablated. These high particle flux precursors lead to fine grained deposited films.

In this paper we will describe the unique femtosecond laser nano-machining facilities and the software that is used to control the Mellos Griot nano-positioners. Furthermore, we will give an over view of many of the applications where this system has been used to produce nano-scale features. For example, we will describe the cutting of NASA aerogel material that is being used to collect dust from a comet. In another application, results will be presented on drilling approximately 1  $\mu\text{m}$  holes in silicon with aspect ratios of  $>30$ . This work represents the first time that such holes have been drilled with such high aspect ratios. Of course this capability has important applications in failure analysis application in the semiconductor industry where one needs to access the electronic lines in chips. Results will be presented on subsurface 3-D data storage in quartz and plastic and our ability to perform 3-D subsurface interconnects in a 3,000 angstrom layer of  $\text{SiO}_2$ . Finally we will present work on the use of the femtosecond laser to produce nano-particle precursors as the source of nucleation sites for the formation of fine-grained thin films of tungsten. Examples of the production of nano-particles will be demonstrated.



## Modeling Laser Ablation and Plasma Expansion for Ultrashort Laser Pulses

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We have developed a one-dimensional Lagrangian fluid model to improve our understanding of laser ablation, of the subsequent plasma expansion and of the ambient gas shock wave dynamics. The model considers several physical processes: absorption of laser radiation (Drude model), hydrodynamic effects [J. P. Christiansen *et al.*, 1972] and thermal conduction [Y. T. Lee and R. M. More, 1984]. The equation of state used is QEOS [R. M. More *et al.*, 1988]. The ablated solid matter and the ambient gas are treated together using the same formalism. (To limit the calculation time, the ambient gas dynamics is usually simplified by assuming that the shock wave, generated in the gas by the expanding ablated matter, is always in equilibrium, so that the Hugoniot relations always hold.)

The model makes it possible to characterize, as a function of time, the conversion of thermal energy deposited by the laser pulse, to kinetic energy, which leads to ablation and to the formation of a shock wave (N-wave) that propagates inside the solid material. The calculated ablation depth and the ablation threshold fluence for simple metals are in agreement with experiments (i.e., less than 1 J/cm<sup>2</sup> for the threshold fluence). The model also clearly shows a stage of explosive boiling [A. Miotello and R. Kelly, 1995] leading to the ejection of high-density fluid particles.

In the case of aluminum, for a fluence of the order of 10 J/cm<sup>2</sup>, the model indicates that the shock wave, generated in air at atmospheric pressure, can reach, at the beginning of its formation, a temperature of several tens of eV and an average degree of ionization of 3 or 4. The expansion of the ablated matter is generally limited to a few mm and has practically stopped after about 10  $\mu$ s. At this time, the axial distribution of the ablated matter is not at all homogeneous. The temperature can vary from ~0.1 eV to ~1 eV while the gas particle density can vary from ~10<sup>18</sup> cm<sup>-3</sup> to ~10<sup>19</sup> cm<sup>-3</sup>.

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## LIBS of Brass Samples with Femtosecond Laserpulses

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The understanding of material removal processes in laser ablation are of significant importance for the correct application of analytical methods like LIBS. Even though laser pulses as short as several 10 ps to 10 ns are used today on a regular basis it is still difficult to study the detailed processes of the ablation mechanism. This is partly due to the time scales which are involved during the light-sample interaction. Material removal takes place on the order of 100 ps which means that a ps-ns laser pulse is still interacting with different, transient thermodynamic states of the solid matter under investigation. This situation changes dramatically if laser pulses as short as 170 fs are used. In this case the laser light interacts only with the electronic subsystem of the solid and all reactions of the lattice of the solid happens after the laser pulse. In this way laser interaction with the solid and material removal are efficiently decoupled.

The aim of our work was to investigate experimentally the ablation of brass samples in argon shield gas by 170 fs laser pulses. The ablation has been studied by time gated optical emission spectroscopy of the evolving plasma. The chemical analysis of Cu-Zn alloys is known to be notoriously difficult [Borisov 1999]. Non-linear calibration plots for both Cu and Zn were observed, and under certain conditions elemental fractionation has been demonstrated. Our experiments at different pressures and fluency demonstrate that even in the case of fs-laser ablation the calibration curves for both Cu and Zn remain non-linear. Linear calibration curves can be constructed by internal standardisation. It is argued that the non-linear behaviour is due differences in the ablation rates which are solely attributed to differences in the material properties. Fractionation has been studied. Within the experimental errors no effect could be found.

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## Characterization Of Azurite and Lazurite Based Pigments

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The most used blue pigments in medieval manuscripts are azurite and lapis lazuli. The first one is a copper based pigment; the colouring compound of the latter is lazurite, a sodium silico-aluminate in a sulphur matrix.

The knowledge of the chemical composition of all the materials employed is fundamental to connote an illuminated manuscript. If trace elements are found, it is also necessary to understand whether they belong to the substrate (paper or parchment), to impurities originally present in the coloring materials, or to moderate quantities of different pigments added in order to obtain a particular hue.

For these purposes it is crucial to choose micro or non-destructive analytical techniques such that the risk of an erroneous attribution of the chemical composition of inks or pigments is minimized.

Micro-Raman and LIBS have been used for the study of azurite and lapis lazuli as well as different mixtures of these pigments applied to parchment to simulate an illuminated manuscript.

The results of our work show the importance of using more than one technique for a good comprehension of the chemical composition of a manuscript. In particular the opportunity of combining elemental composition information (obtained from LIBS) and vibrational spectroscopy information (obtained from Raman) will be fully exploited.

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## Efficient Removing of Foxing From a Medieval Ptolemaic Map Using a Molecular Fluorine Laser at 157nm.

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Using a molecular fluorine laser at 157nm foxing has been removed successfully from a medieval Ptolemaic map published in 1580 A.C. Laser cleaning of stains and foxing from old manuscripts can be very effective at 157nm [1]. There two main reasons for it. First in VUV, there is a complete bond braking of all the organic molecules [2] and hence foxing and organic stains can be removed efficiently at relatively lower laser energy in comparison to other wavelengths. Secondly, the laser light can be focused down to a lithographic accuracy, less than 100nm allowing the highest control ever achieved up to now over the paper area to be cleaned. At 157 nm molecules are disintegrated to small photofragments atomic, diatomic or triatomic, which are flying apart with supersonic speeds. This is because the dissociative excited states of the small organic radicals, occupy the energy range above 6.5 eV (200nm). Mass spectrometry of small pieces of paper, remains of the preservation process, at 157 nm and for moderate laser intensities up to 10 mJ/cm<sup>2</sup>., reveals the presence of the following main photofragments: H<sub>2</sub>, C, N, O, H<sub>2</sub>O, C<sub>2</sub>H, C<sub>2</sub>H<sub>2</sub>, , C<sub>2</sub>H<sub>3</sub>, , N<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>, COH, C<sub>2</sub>H<sub>5</sub>, NO, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>CO, N<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>CH<sub>2</sub>NH, O<sub>2</sub>, C<sub>3</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>6</sub>, CNO. These results could be explained on the basis of the absorption coefficient for the old paper at 157, 193 and 248 nm.

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## **Pigment Identification in Paintings Employing Laser Induced Breakdown Spectroscopy (LIBS) and Raman Microscopy**

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Laser Induced Breakdown Spectroscopy (LIBS) was used in combination with Raman microscopy, for the identification of pigments in different types of painted works of art (Burgio 2000). More specifically a 19<sup>th</sup> century post-byzantine icon from Greece (tempera on wood) and two miniature paintings (tempera on a sea shell substrate) were examined and detailed spectral data are presented which lead to the identification of the pigments used. LIBS measurements yielded elemental analytical data, which suggested the presence of certain pigments and, in addition, provided information on the stratigraphy of the paint layers. Also the major elements, contained in the gold paint present in the objects examined, were determined. Identification of most pigments and of the materials used in the preparation layer was performed by Raman microscopy. Analysis of pigments is of major significance in art conservation, as it can lead to information of great importance in relation to dating, authentication, artistic and historical evaluation of works of art. As shown in this work, the combined use of complementary techniques such as LIBS and Raman microscopy leads to a more complete characterisation of the paintings examined with respect to the pigments used and the structure of the paint layers

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## Spectrochemical Analysis of Metals: Integration of LIFS with LIBS

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The spectrochemical analysis technique of Laser-induced Breakdown Spectroscopy (LIBS) offers a fast, simple real-time method for elemental chemical analysis, normally without the need for sample preparation. As a rule of thumb, the detection limit for trace elements in solid samples usually is of the order 100ppm. In order to improve on detection limits, the technique of Laser-induced Fluorescence Spectroscopy (LIFS) has occasionally been proposed, as an extension to LIBS: atoms in the cooled plasma are probed from their highly populated ground state, using tuneable laser radiation.

Most studies utilising the LIBS+LIFS combination were undertaken in a controlled environment, i.e. in a chamber with the sample being surrounded by a buffer gas (see e.g. the first papers on LIBS+LIFS by Measures and Kwong (1979a, 1979b), and Niemax *et al.* (1990)). However, if LIBS+LIFS is to be used for real-time and on-line analysis it is often not possible to separate the specimen from its source and place it into a controlled environment.

Hence, the main goal of this investigation was to carry out the experiments on samples surrounded by air at atmospheric pressure, using a simple lens - optical fibre system. It is important to note that LIBS is not any longer just a laboratory based measurement technique but can also be applied in the often hostile environments within industry. In some instances it may be impossible to have man access to certain areas, and it is with this in mind that a truly remote LIBS+LIFS arrangement has been set up in our laboratory.

A parametric study was undertaken in which the intensity of the signal was measured as a function of the experimental parameters. Some of the most important aspects that influence the LIFS signal, and thus ultimately the detection limits, were investigated.

The main representative element chosen for our study was chromium (Cr), being an element of importance in a number of chemical, medical and industrial applications. Cr exhibits suitable resonance transitions, accessible by our Ti:sapphire laser system (its 2<sup>nd</sup> harmonic output), and the relevant excited energy levels are very close together (this allows for easy off-resonant fluorescence detection). Furthermore, extensive studies of Cr and plasma evaluations have been undertaken by our group and other researchers; this allows one to make a comparison between the techniques of LIBS and LIFS, and their combination. Other elements investigated in this study include aluminium, (Al), carbon (C), gold (Au) and silicon (Si).

We show that using the combination technique LIBS+LIFS one may in favourable cases significantly improve on detection limits. Specifically this is true in situations where overlapping lines normally severely restrict detection limits. For example, in the case of Si in steels a sensitivity enhancement by a factor of 30-60 was achieved when measuring in air at normal atmospheric pressure.

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## LIBS-LIF-Spectroscopy for the in-situ Analysis of Heavy Metals in Soils

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Laser-based spectroscopic techniques such as laser-induced breakdown spectrometry (LIBS) and laser-induced fluorescence (LIF) have been applied successfully to the chemical analysis of various substances. In contrast to conventional analytical methods like ICP-OES, AAS or SD-OES, they are predestined for online and in-situ applications, because they allow contactless measurements and have essentially reduced requirements for sample preparation.

The determination of heavy metals in soils represents one application for which these characteristics are of great importance. Consequently, numerous publications can be found in the literature on the investigation of the LIBS technique with respect to this topic. In most cases, limits of detection (LOD) in the range of some  $\mu\text{g/g}$  to some  $10 \mu\text{g/g}$  are found [Wisbrun1994], which is sufficient for most of the heavy metals in comparison to regulatory limits. For some critical elements like Cd or Hg, however, LODs below  $1 \mu\text{g/g}$  are required, which has not been demonstrated with LIBS so far. It has been shown that improved detection limits can be achieved by using the combined LIBS-LIF technique in principle [Niemax1990, Gornushkin1997].

In our work, we have investigated this hyphenated technique with special regard to the requirements of the multi-elemental, in-situ analysis of heavy metals in soils. A Q-switched Nd:YAG-laser operating at  $1064 \text{ nm}$  is used for the ablation of sample material and plasma generation. For LIF, analyte atoms are selectively excited within the plasma plume with a second, tuneable laser source operating in the UV wavelength range. The plasma radiation as well as the fluorescence light are guided to a Paschen-Runge spectrometer via fiber optics. This spectrometer is equipped with photomultipliers for all the relevant spectral lines, the signals of which are finally processed by a gateable multichannel integrator and evaluated with a PC.

The LIBS excitation parameters were optimised in such a way that as many elements as possible can be analysed simultaneously with LODs below the German regulatory limits for unpolluted soils merely by the evaluation of the LIBS signal. This was the case for As, Cr, Cu, Ni, Pb and Zn. Additionally, Cd was analysed by the resonant LIF excitation at a wavelength of  $228.8 \text{ nm}$ . We measured a LOD of  $0.25 \mu\text{g/g}$ , which is an improvement by a factor of 24 with respect to the result obtained from the evaluation of the corresponding LIBS signal. It should be emphasised that the measurements were performed at ambient pressure, which is very important for the implementation of the technique for in-situ measurement purposes. In summary, we have demonstrated the simultaneous determination of 7 heavy metals in soil samples with sufficient detection limits. Currently, the LIBS-LIF technique is investigated with regard to the analysis of Hg. Future work will aim at a reduction of the experimental apparatus, which is certainly inevitable for the introduction of an in-situ measurement system.

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## Plasmachemistry in laser ablation processes

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Laser ablation is an exciting field of studies both theoretical and experimental because of its significant potential for formation of atomic, molecular and cluster beams, deposition of thin layers, vaporization of sample material for spectrochemical analysis (Arca et al, 1997). For optimization of these applications it is of great importance the understanding of fundamental processes which determine the laser ablation plume composition. Although numerous studies have been done on plasma plume dynamics there are still questions about the kinetics of chemical reactions to be answered, for example, the influence of the binary compounds formation on the relative amounts of plume species and thus on the sensitivity of laser ablation based spectrochemical analysis.

In the present work based on the results of quantitative spectroscopic diagnostics (LIF in combination with time resolved emission spectroscopy) chemical dynamics in the laser-produced plasmas of metallic (Ti, Al, Pb), graphite samples and Pb containing pressed tablets of soil were examined. The main attention was focused on the elucidation of the role of dimer and oxide formations in controlling of spatio-temporal distributions of different species in the ablation plume.

The Nd-YAG (1064nm, 10ns, 100mJ) and excimer XeCl (308 nm, 10 ns, 10mJ) lasers were employed for ablation. The laser beam was focused on the surface of the rotating sample placed in the chamber with air (helium) atmosphere at pressures varying in the range 0.1 - 760 Torr. LIF spectroscopy was used to detect nonemitting ground state and metastable species ( $C_2$ , TiO, Pb, Ti, Al), while excited species was observed by optical emission spectroscopy.

The results of the spatial and temporal analysis of laser-produced plasmas in the air indicated the existence of the diatomic oxides in the ablation plume both in the ground and in the excited states which are formed from reactions between ablated metal atoms and oxygen. The efficiency of the oxidation reaction depended on the intensity and spot diameter of ablation laser beam. In our experiments, TiO molecules are recorded in the time interval of 570  $\mu s$  after laser pulse and up to 3 mm from the target surface. The maximal concentration of TiO molecules was estimated to be of  $1 \cdot 10^{14} \text{ cm}^{-3}$  at the time of 10  $\mu s$  after the start of the ablation pulse. Comparison of the spatial-temporal distributions of the Ti atoms and excited TiO molecules allowed to find a correlation in their change, which testifies that electronically excited Ti oxides are most probably formed from oxidation of atoms in the ground and low lying metastable states (Burakov et al, 1999).

The possible mechanisms of the chemical kinetics influence on the space-time structure of laser-produced plasma and its evolution in gas environments have been considered. The turbulent mixing of plasma particles with the background gas may be expected from Rayleigh-Taylor instability. The observed more complicated oxidation dynamics may be caused by the local temperature increasing because of a reaction exoergicity and appearing of diffusion and or thermal diffusion matter transfer mechanism at great temperature gradients.

Another possible channel of interplay between chemistry and plume structure evolution was shown to be a condensation and as the first step of this process dimer and cluster formation in the ablation plume. These processes may affect the plume structure due to the nonuniform distribution of plasma species and a spatially (temperature and concentration) dependent reaction rates.

The results obtained are used for improvement of quantitative data of fluorescence analysis of metal traces in environmental samples.

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## Size and Composition Measurements of Individual Ambient Air Particles by Laser-Induced Breakdown Spectroscopy

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The growing recognition of health risks associated with toxic chemicals and fine particulate matter (PM) in ambient air has prompted research activities to further identify understand and solve PM-related problems. Specific research needs include ambient air monitoring (notably real-time monitoring), analyses to characterize the sources of ambient air particulate matter and toxics, and considerations of atmospheric transformation processes associated with these ambient air particles. Experimental data regarding these items form the cornerstone for many other targeted research areas, including evaluation of exposure levels and estimates of risk, emission reduction strategies, and modeling efforts. In particular, data regarding the size and composition of ambient air particles remain at the center of many research efforts.

To fully address the current needs of the environmental community with regard to ambient air fine particulate matter, *real-time* analytical techniques for aerosol analysis must be developed and made available. Real-time instruments will provide the ability to collect the large numbers of aerosol data sets required for understanding the often-complex issues associated with ambient aerosols. This paper will focus on LIBS as a novel means to address critical needs in the real-time monitoring and characterization of ambient air particulate matter.

In this work, the LIBS technique is evaluated as a means for quantitative analysis of the size, mass, and composition of individual micron to submicron-sized aerosol particles over a range of well-characterized experimental conditions, including the on-line analysis of ambient air. Conditional data analysis is used to identify LIBS spectra that correspond to discrete aerosol particles. The size distributions of particle source flows are presented as measured using the LIBS technique for calcium, magnesium, and chromium containing aerosols. The resulting size distributions are in very good agreement with independently measured size distribution data. In addition, the accuracy of the LIBS technique for the interference-free analysis of different particle types is verified using a binary aerosol system. Ambient air measurements are presented for a number of metallic and mineral-based species. A lower size detection limit of approximately 175 nm is reported for the calcium and magnesium-based particles, which corresponds to a detectable mass of approximately 3 femtograms.

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## Analysis Of Fluorine, Chlorine, Sulfur, phosphorus and Carbon in Air By Time Resolved Laser Induced Breakdown Spectroscopy

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Time REsolved Laser Induced Breakdown Spectroscopy method (TRELIBS) has been developed at the Centre d'Etudes du Bouchet (CEB), in France, to answer to real necessity of sensitivity and selectivity in detection of gases or polluted surfaces. Indeed, chemical weapons such as mustard gas and neurotoxics have been banned in most countries and the CWC treaty will be ratified at the end of 1997 by more than 60 States. Nevertheless, these weapons are still stored in many arsenals. Consequently, their control and destruction are today at the heart of many international projects.

Our goal is to propose new tools to detect in a very short time (1-10 s), low concentration (close to 1-10 ppm) of these kinds of toxic molecules both for military and civilian needs. The main advantage of the TRELIBS method is that, without laborious chemical preparation, it especially provides direct analysis of gases or solids. Only optical access to the sample is required, and sample contamination-induced risks are minimal.

The main objective of this study is to obtain the detection limit thresholds for atomic elements such as fluorine, sulfur, phosphorus, chlorine and carbon in air, because these elements are present in hazardous gases or in the organic compounds which are used as chemical weapons such as nerve agents and blister agents.

In our study, chemical compounds such as CFC or SF<sub>6</sub>, diluted at atmospheric pressure in air are selected to recognize them. Thus, our work has been focused on the ability of the TRELIBS method to analyze those complex molecules without any sampling procedure. Our results point out that F, Cl, S, P and C can be identified and quantified by TRELIBS, with a short analysis time, by using their atomic emission lines in the near ultraviolet to near infrared spectral ranges. One of the main results is that we are currently able to determine the partial molecular formula of molecules such as CFCs. This result demonstrates that very stable molecules (SF<sub>6</sub>, CF<sub>4</sub>) are completely destroyed in the high temperature plasma induced by laser. However, the minimum detectable concentrations are the second challenge of this technique. The experimental results have shown detection limits for fluorine and chlorine close to 20 ppm without signal treatment, while for the sulfur detection the limit threshold is presently only 1500 ppm. We do have to increase by a factor of 10 the sensitivity of the system, in order to respond to the detection requirements for toxic agents.

Our goal is now to establish a miniaturization for the in-situ analysis in military and civilian applications, to reach lower thresholds requested because of the high toxicity of CW agents and to develop the potential industrial applications of the LIBS technique. Indeed, LIBS method is very promising for industry, where on-line analysis is requested, and it can be applied to a variety of environmental analyses as well (biological and chemical pollutions in air and soils).

## Application of LIBS into Heavy Metal Measurement in High Temperature Flue Gases.

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To realize the real-time measurement of trace metals in flue gas under high temperature condition by laser induced breakdown spectroscopy (LIBS), intensities of line spectra depending on plasma temperature are studied experimentally using aerosol and particle feeding systems.

The application of LIBS to the analysis of gas component has been developed for various fields, such as waste incineration and coal combustion. (e.g. J. P. Singh 1999) The technique of LIBS has the merit of offering a fast, simple and real-time method of elemental analysis. However, the practical condition to analyze trace element may vary in temperature, pressure and coexisting materials. LIBS spectra themselves are much affected by them. Then, to quantify the concentration of elements in gas using simple calibration curves, calibrations must be done under the same condition as the actual environment. This fact makes LIBS technique much inconvenient to analyze the hot flue gas. To overcome this difficulty, we are focusing on the plasma temperature as representative parameter to generalize the calibration data. If a number of calibration curves are provided over a wide range of plasma temperature in advance, the valid calibration data can be selected for a given plasma temperature.

Ultrasonic nebulizer system was developed to prepare the sample gas where aerosol of metals was entrained at strictly defined concentration. It was used to get standard calibration curves between line intensities and absolute concentrations of elements in gas, and to find the detection limit for each metal. Particle feeding system, in which piezoelectric vibrator was utilized for driving particles with constant feeding rate, was also produced to examine the LIBS spectra emitted from particulates suspended in gas. Minerals containing iron were used as sample particles in this study and then Fe line intensities could be applied for the estimation of plasma temperature via a Boltzmann plot. Time evolution of the temperature of laser induced plasma was observed and it was found to be more than 7000 K during a few of tens microseconds after breakdown. The relative intensities of metals to the emission from matrix elements in particles were also measured to quantify the amount of metals included in particles.

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## In-Vessel Material Analysis of AGR Steam Generator Tubes Using a Fibre-Probe LIBS Instrument

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A novel-design instrument based on Laser-Induced Breakdown Spectroscopy (LIBS) and incorporating a 75 metre optical-fibre umbilical and remote probe has been used to remotely analyse steam generator tubing inside the pressure vessels of Advanced Gas Cooled (AGR) nuclear power stations. The instrument was deployed successfully at Hunterston B and Hinkley Point B stations during July and August 1999 and used to carry out semi-quantitative measurements of the copper content of the 316H stainless-steel steam generator tubes as part of a reactor outage inspection programme.

The LIBS instrument, illustrated schematically in figure 1, consisted of a control module linked by a 75 metre umbilical to a specially designed pneumatic probe. The control module, located in a cabin above the reactor pile cap, contained the Q-switched Nd:YAG laser, an optical spectrograph incorporating a time gated ICCD detector, the fibre launching optics and an industrial portable PC. The umbilical was used to provide mechanical protection for the optical fibre and to deliver compressed air to the pneumatically operated probe. The probe was designed to fit each of the 528 bifurcations per reactor and to be easy to deploy within the confines of the superheaters (figure 2). The umbilical was fed into the vessel via the man-access route and deployed in each of the twelve superheaters (figure 3).

An overview of the development and deployment of the LIBS instrument will be presented.

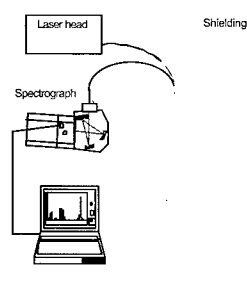


Figure 1. Schematic of fibre-probe LIBS system

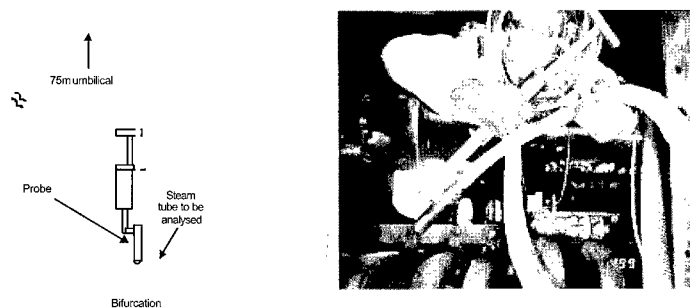


Figure 2. Fibre-probe deployment in an AGR superheater

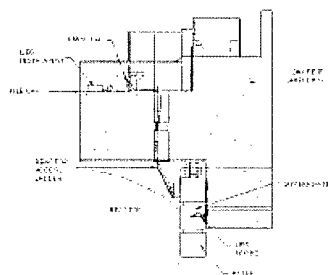


Figure 3. Sectional view of AGR vessel showing route taken by umbilical

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## **A Direct Push Sensor Probe for Real-Time *In Situ* Measurement of Metals in Soil Via Laser-Induced Breakdown Spectroscopy (LIBS)**

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Contamination of soils by heavy metals from anthropogenic sources related to mining, industrial and military activities is a problem worldwide. Traditionally, the delineation metal contaminated soils have relied on collection of soil samples followed by subsequent laboratory analyses. Because lab results are often not available for several weeks after the sampling effort, complete delineation of the impacted area is often a slow and expensive. Frequently, additional sampling efforts are required to complete the characterization of the site. In response to this need we have developed and field-tested a LIBS sensor probe that can be pushed directly into the soil with a truck mounted hydraulic system. The sensor system is capable of making very high resolution vertical measurements (cm spatial scales). Because data is available in real-time, sampling plans can be modified as the as the data is being collected, to more effectively delineate the extent of the contamination.

In this paper, we will present a technical overview of the fiber optic-based LIBS sensor system (Theriault et al., 1998). Details will be provided on a unique probe design in which the plasma is generated on soil in contact with a sapphire window on the probe. This design maintains critical lens to sample optical geometries necessary for optimal plasma generation. In addition, it eliminates problems that may result from loosely consolidated soil and dust that can degrade the performance of "open-beam" systems that use optics that are recessed from the surface of the probe. (Miles et al, 1997).

Results will be presented from several field tests of the LIBS sensor system was used to make measurements at sites contaminated with lead, chromium and other metals. The utility of the sensor system for rapid field screening will be demonstrated by comparison with traditional laboratory measurements. Finally, affects of variable soil matrix and soil moisture conditions on sensor performance will be discussed.

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## Development of LIBS Experimental Set-Up for Remote Analysis of Solids and Liquids.

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A problem facing some manufacturing groups, and particularly in the nuclear fuel cycle, is potential contaminations during the production of fuel, and research is going on for suitable *in-situ* analytical technique to control solid materials in an hostile environment. Ideally, these developments must provide reliable and fast measurements in various areas of the nuclear fuel cycle. A Laser Induced Breakdown Spectroscopy (LIBS) set-up devoted to *in-situ* measurement of trace elements in radioactive solid materials has been designed.

The possibility offered by LIBS to investigate impurities at concentrations around 100 ppm, rapidly (i.e. 5 s to obtain a spectrum section) *in-situ* at atmospheric pressure without any preparation and little effluents (the amount of matter destroyed by laser ablation is low) in two nuclear solid materials,  $\text{UO}_2$  and  $\text{PuO}_2$ , was demonstrated. Detection limits of about 100 ppm were found in both matrices for the impurities observed.

Laser Induced Breakdown Spectroscopy has also been tested for elemental quantitative analysis remotely in liquids. Quantitative results on the sample compositions were obtained by laser ablation on the surface. An original set-up is proposed which can allow on-line measurements in liquid materials, but for the moment no experiment has already been carried out on radioactive liquid samples. Twelve elements have been studied in two different liquid matrices : water and oil in order to evaluate the ability of the analytical technique for different types of liquids. Detection limits and reproducibility are discussed. Moreover, the utilisation of an echelle spectrometer for plasma analysis has also been tested.

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## Quantitative Analysis of Trace Metal Ions in Water and Ice using LIBS

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Laser spectral microanalysis has become a very powerful technique for rapid, spot analysis of solid target materials. Although only minute amounts of solid material are typically vaporised trace elements can be detected at concentration levels as low as a few parts per million. Much less attention has been paid to LIBS analysis of liquid samples; largely this is because a number of alternative techniques are available which are superior to LIBS in their sensitivity. In addition, some experimental problems may be encountered when irradiating a water surface with a pulse repetition rate of 10Hz or more, as is typical for the lasers routinely used in LIBS analysis today.

In this presentation, we report studies on LIBS trace analysis of aqueous samples, both in their liquid and in solid (frozen) form. The experiments were carried out using a range of different laser wavelengths, ranging from the UV through the visible to the infrared (the various harmonics of a Q-switched Nd:YAG laser, and radiation from a Q-switched CO<sub>2</sub> laser).

In modern water analysis, two types of trace species are of interest, namely organic and inorganic molecular pollutants, and potentially toxic metal ion species. By its nature LIBS is nearly exclusively restricted to elemental analysis. We have analysed a range of water samples for traces of metallic ions, including most of the alkali and alkaline earth elements, and a few metals notorious for their potential toxicity. The measurements were carried out using experimental set-ups suitable for petri dish and direct on site analysis, with remote capability (see Samek *et al*, 2000). The detection limits obtained are consistent with those reported by other research groups (see e.g. Knopp *et al*, 1996) ranging from a few hundred ppm (for uranium) down to a few tens of ppb (e.g. for lithium).

In addition to investigating aqueous solutions in their liquid aggregate state we applied a quick-freeze procedure to generate well-defined slabs of ice. Such solid specimens are much easier to handle than liquid samples while they maintain the inherent homogeneity of a liquid solution. Measurements were carried out for a range of metal ions, and results from liquid and solid water samples are being compared respective sensitivity and reproducibility of the analysis.

In addition, the approach easily lends itself to the analysis of real ice and snow samples, e.g. from the arctic ice cap, to determine trace amounts of various elements in the ice with spatial resolution. This analysis can then be used to link the spatial elemental concentration data to a time scale of environmental influences, provided the elemental migration processes in ice can be addressed quantitatively (see Livingston and George, 1999). Furthermore, micro-particle and colloid enclosures can easily be studied, maintaining some information on their actual location and particle size. Both aspects are briefly addressed in this study.

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## Depth Profile Correction in Multilayered Materials Drilled by Laser Pulses

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The effective formation of small size holes (laser drilling) and the laser ablation of a thin layer of a material, carried out jointly with an analysis of the luminescence spectrum of a plasma (LIBS), make it possible to determine the depth profiles of the concentration of the elements in ablation craters in inhomogeneous and layered materials for different rates of variation of the thickness of the ablated layer per pulse.

However, a comparison of the profiles of layered samples, obtained with the aid of a LIBS technology and by the glow-discharge technique, showed that in the first case the profile is smoothed out to a greater extent and that the layer boundary is not quite so distinct as in second one. An experimental study has shown that the principal reasons for this discrepancy are the change in the plasma parameters as the crater becomes deeper and also the significant difference between the intensities of the spectral lines of the elements when layers of unlike materials are perforated.

An algorithm for the correction of the atomic lines intensities in the LIBS spectra was developed for measured of the depth profile of the elemental composition of multilayered materials in an ablation crater. The application of this algorithm made it possible to eliminate the profile smoothing effect as a consequence of a change in the LIBS line intensity as the crater becomes deeper. The approach developed was tested experimentally. The correction of the profile is illustrated by an measurement of the thickness of a diffusion layer of zinc-plated sheet steel before and after its heating at 452 C.



## Enhanced Laser-Induced Breakdown Spectroscopy using Sequential Fourth-Harmonic and Fundamental Nd:YAG Laser Pulses

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Laser-induced breakdown spectroscopy (LIBS) usually combines material sampling and excitation in a single step. Yet, these two forms of laser-matter interaction do not have the same wavelength dependence. Most analytical techniques relying on the laser strictly for sampling (e.g. LA-ICP-MS) use ultraviolet (UV) radiation, which is strongly absorbed by the material, but less so by the plasma formed in front of the target. This leads to a more efficient ablation, with minimal selective vaporization and better spatial resolution (Geertsen et al. (1994)). The opposite situation holds for near-infrared (NIR) radiation: energy absorption in the plasma through inverse Bremsstrahlung is more efficient than in the UV, and leads to a hotter and brighter plasma.

The ideal approach for materials analysis by LIBS should therefore consist of separating the two steps of sampling and excitation, and using the most appropriate laser wavelength for each. This amounts to adopting a double-pulse approach where a UV pulse (for ablation) is followed by a NIR pulse (for plasma heating).

A double-pulse approach with both pulses in the NIR (at 1064 nm) has already been shown to increase analytical sensitivity (Sattmann et al. (1995), St-Onge et al. (1998)). In such a scheme, the second pulse is absorbed in an expanding preplasma. The result is a larger volume of hotter plasma, and thus a larger integrated intensity. Taking this as a starting point, and based on the above reasoning, we evaluated experimentally a new embodiment of the double-pulse approach where the wavelength of the first pulse is lowered into the UV (at 266 nm). This report contains the first results of such an investigation, performed on metal alloys.

As implied above, the ablation characteristics should be determined solely by the UV prepulse. This goal was partly achieved. From studying the ablation craters and the surrounding surface, it was deduced that the plasma formed after the first pulse succeeded in limiting the extent to which the NIR beam (colinear with the UV beam), or the subsequent plasma, interacted with the surface.

Moreover, addition of a small UV prepulse resulted in an enhancement of line intensities by a factor 5 to 20, depending on the line and on the NIR pulse energy. The enhancement was larger for ionic lines and in general for emitting states with higher excitation energies. Accordingly, excitation temperatures and electron densities were found to increase when using the UV prepulse. The intensity enhancement was also larger for stronger NIR pulses. For example, adding a 5 mJ UV prepulse 2  $\mu$ s before a 100 mJ NIR pulse resulted in line intensities an order of magnitude larger than with the 100 mJ NIR pulse alone, even though the total energy was almost the same. As a consequence, detection limits can be lowered significantly.

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## EcLIPS – A Versatile Echelle-Spectrometer System Dedicated to LIPS Applications

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A major reason for the increasing interest on LIPS in recent years is the improved instrumentation. Significant progresses were made in the field of laser technology in terms of long-time stability, handling, service, and size. As well modern detection CCD-cameras with high sensitivity, low noise and easy handling can be considered as standard detection systems for LIPS, which boosted its development. Only the spectroscopic resolution is mostly still carried out with Czerny-Turner spectrometers, which hardly exploit the full capacity of modern CCDs. Its one-dimensional spectra reveal a maximum number of channels between 500 and 2000, depending on the CCD chip size, limiting either spectral resolution or coverage, thus leading to a limited multielement capability. Only in recent years first combinations of echelle-spectrometers with ICCDs are developed for LIPS applications. After experimental systems consisting of ICCDs adapted on echelle spectrometers initially designed for other detection systems (Haisch et al., 1998; Bauer et al., 1998) meanwhile two systems are commercially available (Löbe et al., 1998; Lindblom 1999). Both systems include the ICCD detector.

We constructed a universal stand-alone echelle spectrometer, which can be combined with a wide range of intensified and non-intensified cameras. As most LIPS laboratories are equipped already with ICCDs the set-up can be up-graded with low mechanical as well as financial effort. The modular construction allows the selection of the spectral range between 200 and 900 nm, simultaneously covering 200 to 400 nm with a constant resolution  $\lambda/\Delta\lambda$  of 15000 to 20000 (actual res. on 4 pixels). Also a VUV-option, starting from 160 nm, is being constructed. A further aim of the optical design was the high optical throughput and small size, allowing even the construction of portable systems (400 mm × 200 mm × 200 mm).

The construction of the system and first results of LIPS experiments with Intensified and non-intensified camera systems are presented. In the standard configuration (220 – 400 nm,  $\lambda/\Delta\lambda=15\,000$ ) we were able to simultaneously quantify up to 50 elements with concentrations down to few ppm. Also with a non-intensified camera system we achieved surprisingly well-resolved spectra with pronounced emission lines, which can be explained eventually with the high spectral resolution of the system.

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## Depth-resolved Profiling of Galvannealed Steel Samples by Laser-Induced Breakdown Spectroscopy

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Laser-Induced Breakdown Spectroscopy (LIBS) is a suitable and powerful method for direct in-process measurement of elements concentration and depth-resolved profiling in material analysis and metallurgical applications.

A low cost laser induced breakdown spectroscopy system was developed. This system is composed by a Nd-YAG laser (irradiance:  $\sim 10^9 \text{ W/cm}^2$ ), an optical focusing system, a polychromator and an optoelectronic processing device. A linear CCD camera, data acquisition electronics and associated control software were specifically developed to capture and process the plasma's spectral lines intensity. The technical characteristics and mechanical design of the system were oriented to "in situ" surface analysis of solid samples. Using an optically transversal remote sensing experimental setup, it is possible to select an optimized place, through plasma's plume, to increase the spectral signal to noise relationship. This transversal spatial resolution substitutes the necessity to use a time-resolved spectroscopy system.

The intensity of plasma's spectral lines depends not only on the specific element concentration but on the power density and local plasma temperature too. To minimize the influence of the plasma's spectra line intensity changes with beam penetration and to improve the depth resolution, a normalized algorithm was proposed and tested. The advantages of this approach in LIBS technique, to resolve qualitative and quantitative analysis of multilayered samples depth profiles, were demonstrated.

Different types of galvannealed steel samples were quantitatively studied by monitoring the specific Zn and Fe emission intensities with depth profiles. Using a differential scan calorimeter (DSC), the galvannealed steel samples were thermally modified. Their interfaces distributions changes were studied and correlated by LIBS deep-profile analysis, by energy dispersion spectroscopy (EDS) and scanning electron microscopy (SEM). These techniques allowed the estimation of the ablated mass per shot and the penetration rate. Possibilities of employing the developed LIBS system to control metallurgical processes are also discussed.

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## New Instrumental Approaches for the Lateral and in Depth Characterization of Surfaces and Interfaces using LIBS

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Laser-induced breakdown spectrometry (LIBS) is considered as a promising technique in terms of the outstanding capabilities to perform fast and accurate analysis in air at atmospheric pressure without limitations in sample size or nature. Recently, LIBS is being explored as an alternative technique in surface analysis due to its capabilities to furnish information on the lateral and in-depth distribution of the constituent elements of a sample at the micro- and nanometric level.

Using LIBS for traditional compositional mapping, a selective image of the sample depicting the distribution of a given element is easily obtained. To date, detailed spatial information by the so-called imaging-mode LIBS has been achieved by point-to point mapping using a spherical lens focusing system, at the cost of increased measurement time and data storage requirements. An alternative approach of obtaining images using LIBS involves exploring the two-dimensional capability of CCD detectors. In this type of system one dimension of the detector is reserved for light dispersion (providing spectral information), while emission from different parts of the surface is effectively focused onto the second dimension of the CCD (providing spatial information). Fully advantage of this approach can be obtained if the laser is focused to a microline at a energy exceeding the plasma threshold fluence along the microline, and collecting the plasma formed in a direction parallel to the spectrometer entrance slit. In this way, each ablated location in the sample will generate a signal at a defined height in the slit. In this communication, the microline-imaging LIBS approach is presented and performance parameters for generation of surface chemical images are discussed.

In-depth analysis of solid samples is also a fashioned LIBS application. However, the lack of homogeneity in the beam-energy distribution or the redeposition of ablated material in the crater somehow is limiting the number of applications. In this communication, several examples demonstrating the capability of LIBS to perform depth profiles with nanometric resolution will be presented. The effect of imperfect focussing or irregular beam distributions will be discussed as well.

## Progress in Laser-OES

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There are numerous examples throughout industry where materials analysis is required, be it for process control, effluent monitoring, control of product quality or plant integrity and condition monitoring. Besides, the time and costs reduction for control contributes significantly to both the improvement of product quality and the rationalization of the production process.

To cope with the need for rapid low cost control during process, the switch from conventional specific instruments to the possibility to operate on-site global control (elementary composition, conductive and non conductive materials, defects characterization) adjacent to the production line is in progress. In this respect, the potential of LIBS has basically been demonstrated <sup>(1-3)</sup>, and research developments need to be industrialized.

With the intention to provide the required solutions to the steel making industry, and based on the wide expertise acquired in this field with spark spectrometry, an industrial laser spectrometer has been developed. Based on the use of a Q-switched Nd:YAG laser, a tight ablation/excitation stand, translation and rotation possibility for the beam focusing unit, and the use of an adapted light collection and detection unit including the VUV spectrum, the possibility to carry out elementary and defect control of all elements of interest (120–800 nm) in the steel industry is investigated.

In a first approach, calibrations of a number of elements (P, S, C, Cu, Mn, Ni, Cr, Mo...) obtained for trace analysis with this LIBS spectrometer demonstrated similar figures of merit than those obtained with modern electrical spark OES, limits of detection as low as 1 ppm could be measured for C and S for instance.

The 50 µm lateral resolution provided by this laser mounting also demonstrated some interesting features in the field of defects characterization. The mapping (14×14 mm<sup>2</sup>) of an inclusion line points out the possibility to obtain information very close to the surface investigating methods (optical microscopy, SEM...), with fast chemical information: a discontinuous inclusion line, preliminary observed with optical microscopy, could be detected with LIBS whereas it was not possible with the classical electrical spark mapping, or would have taken about five times more time to be investigated with SEM based techniques, not adapted to industrial on time process control.

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## On the Validity of LTE Formulations Applied to LIBS

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Emission spectroscopy of laser induced plasmas has been applied to the qualitative and quantitative analysis of a variety of targets: solids (K.Y.Yamamoto et al, 1996), liquids (D.A.Cremers et al, 1984) and gases (C.Lazzari et al, 1994).

It is evident from the experimental observations that the recorded spectra do not obey Planck distribution. In fact, the first distribution to depart from equilibrium is that of radiation.

For particle distributions, the prediction of a minimum electron density assuring Local Thermodynamic Equilibrium (LTE) in relatively cold plasmas remains a difficult task. Generally, authors rely on simple ingredients leading them to assume LTE or Non-LTE in the irradiated medium. However, LTE expressions are used for want of anything better. The advantage of LTE is its simple formulation and the reduced set of data needed. A more complete model should take into account many other processes in addition to the collisional ones.

The present contribution is dedicated to the theoretical investigation of the departure from LTE using extensions to Saha and Boltzmann equations generalized to include the radiative processes. We considered a screened atomic structure and a set of collisional and radiative processes. We develop a series of formulae for line intensities and line intensity ratios that are valid for LTE as well as for Non-LTE plasmas.

We show that ignoring time-dependency and molecular processes and considering only some atomic processes that the plasmas found in the conditions of a few eV and at electron densities of about  $10^{18} \text{ cm}^{-3}$  are in LTE. Sensitive departure from equilibrium occurs at much higher temperatures at this same electron density.

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## Ozone Production in Early LIB Plasma

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The objectives of this work were to study the fundamental processes relevant to the formation of the laser induced plasma and, as the consequence, to improve the analytical potential of laser-induced plasmas in terms of accuracy and precision of analysis. Our emphasis was on the early stages of plasma development. First, we measured plasma continuum (0-40 ns delay) in 190-

390 nm spectral range. A series of plasma spectra from a Zn target is shown in Fig.1. One specific feature of the spectra is immediately obvious: a large absorption band gradually develops at about 250 nm. We have identified this band as the well-known Hartley ozone band. It is not surprising that ozone is created in large amounts under the action of the strong UV radiation emitted by the continuum from the hot plasma. Within the first 10-20 ns, the plasma temperature is about 12000 K which corresponds to a

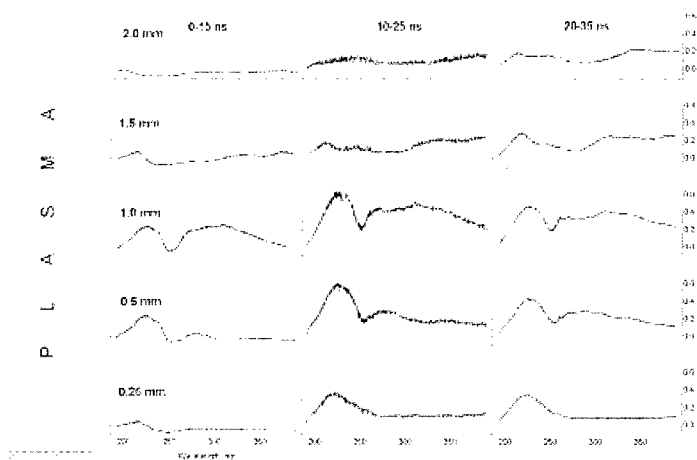


Fig.1. Spectral, spatial, and time resolution of plasma continuum

maximum of the blackbody function at ~220 nm. This plasma is a very bright UV source. At later times (100 ns-1000 ns), when a structured spectrum is developing, the photochemical production of ozone can be continued by strong UV atomic or ionic lines. The amount of observed ozone was sometimes so large that it caused baseline absorption in the early plasma.

Besides measuring ozone in a pulsed mode, we also studied steady-state ozone production by igniting sparks on different targets and in air. Two laser sparks were used in these experiments: one spark on the target which produced ozone in a small confined volume, and the other spark in the air (or argon) which served as a broadband light source. The relative rates of production/depletion of ozone were estimated.

We also obtained shadow images of the early laser plasma. An enlarged frequency-doubled dye laser beam was tuned in resonance with the maximum of the ozone absorption band (250 nm). This beam was guided through the region of laser breakdown at different delay times relative to the moment of the plasma ignition. Some interesting features were revealed concerning the shock wave propagation and the change in refractive index on and within the plasma boundaries.

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## Study of The Effect of Loss Processes in Laser-Induced Breakdown in Nitrogen by a Wide Range of Laser Wavelengths

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In the present work a study is performed to investigate the effect of loss processes on the threshold irradiance when molecular nitrogen over a pressure range 400-760 Torr is irradiated with the first four harmonics of a Nd:YAG laser radiation at wavelengths 1064, 532, 355 and 266 nm with pulse duration 8.5, 7.5, 6.5 and 5.5 ns respectively (Davis et al. 1991). The analysis is based on a previously developed electron cascade model (Evans and Gamal 1980) which solves numerically the time dependent Boltzmann equation for the electron energy distribution function, simultaneously with a set of rate equations describing the rate of change of the excited states population. The model considers the electron energy gain through inverse Bremsstrahlung absorption and electron generation by multiphoton ionization and collisional ionization of ground state as well as the formed excited states. Loss processes which deplete either the number of the electrons (i.e. electron diffusion, recombination, etc.) or their energies (i.e., dissociation, vibrational excitation, rotational excitation, etc.) are considered in this analysis.

For realistic computational results the exact correlation between the electron energy and cross-sections or rate coefficients of each of the physical processes encountered in this model is taken into account.

The effect of loss processes is investigated as a function of the threshold irradiance for each laser wavelength. In doing so calculations are carried out to compare the electron energy distribution function and its parameters (time evolution of the electron density, ionization rate and electron mean energy) for two values of gas pressure examined experimentally namely 400 and 760 Torr.

These results revealed that vibrational losses act to deplete electrons with low energies (<4 eV). More over dissociation of molecular nitrogen results in a depletion of the high energy electrons (>11 eV). On the other hand electronic excitation enhances the rate of electron generation through stepwise ionization processes (mainly multi-photon absorption). These processes showed very effective contribution over the whole wavelength range studied experimentally.

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## On The Existence Of Equilibrium Conditions In LIBS Plasmas

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A large effort is at the moment dedicated to the understanding of the properties of LIBS plasmas due to their wide use as analytical tool for determining the concentration of metals under different conditions.

The accepted idea is that this kind of plasmas generated by the interaction of ns laser with targets of different nature fulfills equilibrium conditions i.e. the population densities of the different species satisfy Saha equations while Boltzmann distributions describe the concentration of electronically excited states and Maxwell laws describe the electron energy distribution functions. These assumptions derive from the high electron densities existing in LIBS plasmas. Recently however these assumptions have been criticized due to the short temporal scales involved in the process. We refer in particular to the expansion time of the plume generated after the laser interaction and to the times necessary to the population densities of excited states to reach quasistationary conditions. Moreover the times necessary to build up quasistationary electron energy distribution function are not so short as commonly accepted.

All these times can merge in the same temporal scale determining non equilibrium conditions in LIBS plasmas with consequences on the applicability of the technique.

This kind of problems has a long history in the plasma community since they occur in completely different situations. We refer in particular to short transient plasmas generated by time varying voltages as well as to the plasma dynamics through nozzles.

The present contribution will try to answer to some of the main problem of the LIBS literature about the existence of equilibrium conditions during the short transient in which the time resolved atomic spectra are monitored. To this end we will use a time dependent collisional radiative model for the population densities of excited states coupled to a time dependent Boltzmann equation for the electron energy distribution function. Results for atomic H, taken as an example, will be discussed for plasma conditions typically met under LIBS plasmas.

## Temporally – and - Spatially Resolved Optical Emission Spectroscopy in Plasma Assisted KrF Excimer Pulsed Laser Deposition of TiO<sub>2</sub> Thin Films

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Plasma assisted KrF excimer pulsed laser deposition (PA-PLD) of TiO<sub>2</sub> thin films with biased substrate is investigated by temporally - and spatially - resolved optical emission spectroscopy over a wide range of oxygen pressure (from 10<sup>-6</sup> to 10<sup>-1</sup> torr) and laser fluence (from 0.8 to 6 Jcm<sup>-2</sup>). A number of characteristic titanium Ti lines (from neutral excited species TiI and from single ions TiII) occurring as result of the laser irradiation interaction with targets from TiO and TiO<sub>2</sub> materials are observed. A time evolution of Ti spectral lines intensity and broadening are measured to determine an atomic and ionic state distribution functions (ASDF) and (ISDF) and to estimate electron number density depending on time on various distances from targets. Emission spectrum of the laser-induced plasma (LIP) differ very slightly when conventional PLD and PA-PLD techniques are used. ASDF and ISDF can be represented, in good approximation, in a Boltzmann form. The values of temperatures appropriate to the measured ASDF and ISDF, of the LIP expansion (from 100 to 300 ns from beginning of the laser irradiation interaction with targets) is appreciably differed. Variation in temperature of TiI is insignificant in time, and it is varied from 11000 K to 8000 K, whereas temperature of TiII is markedly decreased from 28000 K to 15000 K. Change of oxygen pressure leads to insignificant variations in spectral intensities of TiI and TiII lines. With increasing laser fluence from 0.8 to 2.5 Jcm<sup>-2</sup> the temperatures of TiI and TiII grow within the limits of 7000 K to 10500 K and slightly decrease with oxygen pressure. An interrelation between the time evolution spectral intensities of TiII and that of spectral lines widths and profiles of TiI and TiII is observed. There exist two stages of the LIP expansion. At the initial stage of the plasma expansion from 100 to 250 ns spectral lines profiles of TiI and TiII are dramatically changed from Lorentzian to Voigt profile. The appreciable reduction of TiII line intensities is accompanied as abrupt diminution of linewidths. Basic mechanism of broadening of Ti lines is a quadratic Stark-effect. The electron number density defined from the quadratic Stark-broadening of the spectral lines as the function of gate delay is reduced from 3·10<sup>15</sup> to 10<sup>15</sup> cm<sup>-3</sup>. At a later stage of the plasma expansion from 200 ns to 400 ns profiles of the spectral lines are approximately Voigt profiles. The spectral lines widths and intensities of TiI and TiII decrease more slowly in time in comparison with their values at the initial stage of the plasma expansion. The basic mechanism of lines broadening is changed. Lack of experimental data does not allow to make a unequivocal conclusion for the benefit of possible mechanisms of lines broadening, which according to numerical estimations can be a spectral line self - absorption or resonance mechanism. The lower value of the electron number density for existing of local thermal equilibrium (LTE) is equal to 6·10<sup>15</sup> cm<sup>-3</sup> that is larger than that measured in this experiment. The low measured values of electron number density and distinctions between temperatures of TiI and TiII testifies that LTE model is not valid for our experimental conditions.

## **Spectroscopic Analyses of Laser Induced Oxidation Enhancement in the PLD Process**

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Pulsed laser deposition (PLD) is a method to obtain thin films with different compositions. In case of multi-component oxide materials, as superconducting materials, the main problem is to have in the as-deposited layer the proper content of oxygen.

In this reason we have developed a method designed to reduce the oxygen deficiency in the as-deposited YBCO superconducting thin films. A IR laser beam focused in front of the target, simultaneously with the UV laser beam, irradiates the buffer gas in which UV laser ablated plume evolves. The aim of this transversal irradiation is the oxygen dissociation and atomic oxygen formation. Temporal evolution of ionic, neutral and oxides lines is analysed in the 400 - 620 nm region.

The emission spectrum of YBCO plume, monitored at different times in the plasma evolution, evidenced a rich line spectrum superimposed on a continuum background. Lines of YI, YII, BaI, BaII, CuI, CuII, YO, BaO, CuO appear in the emission spectrum. In case of laser ablation of the target with a supplementary IR laser focused at 3 mm in front of the target on the expansion axis of the plume, an enhanced emission is observed in the spectral region of the oxides lines. This means that the oxides quantity in the plume evolution enhances in the region of the IR laser radiation focal region, in spite of the fact that laser intensity in the focus is lower than the breakdown threshold of the background gas.

It is known that in the presence of background oxidising gas, plumes species attenuation will occur, caused by elastic scattering and reactions during interaction with the buffer gas. Also, for high background gas pressures ( $>0.1$  mbar), the plume gas interaction leads to the formation of a nonsteady shock wave. The gas phase oxidation efficiency depends on the buffer gas nature (dissociation energy, electron affinity), ablation species ionisation potential and the kinetic energy of the plume species involved in the oxidation reactions. In the IR irradiation region, the oxygen molecule will dissociate under the effect of the large electric field, leading to atomic oxygen and ozone formation, species with enhanced oxidation efficiency.

The amplification in the oxide emission can be explained by two factors. We may assume that, following a collisions mechanism, the enhanced emission is due to an induced overpopulation of the excited states on the basis of the depopulation of the ground states. But there was no evidence of such a phenomenon on the neutral and ionic lines. So, we can conclude that the enhanced oxide emission, specially at later times, where atomic and ionic emission is low, is due the oxidation in gas-phase interaction with the dissociated oxygen.

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## **Laser-Induced Breakdown Spectrometry for Characterization of Surface Stoichiometry of Coated Samples Prepared by Pulsed Laser Deposition**

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Surface treatments and coatings are commonly employed by manufactures throughout the world for increasing the performance, productivity and longevity of tools and components. The desired coating properties and required performance vary from application to application. Thus, the necessity to control the quality across a surface is increasing. It is therefore crucial the application of the latest technologies to obtain information about interfacial morphology, composition, structure and properties of the surface. However, the main drawback is that the most of surface analysis techniques require a vacuum system.

Recently, the use of laser induced breakdown spectrometry (LIBS) as an alternative method for surface characterization has been demonstrated. The sensitivity, selectivity and versatility of this analytical technique makes it ideal for surface analysis and depth profiling of manufactured samples.

This work shows the capability of LIBS for quantitative surface characterization of coatings. Samples used for this study consisted of coatings of manganin (Cu, Ni and Mn) on a Si substrate and were prepared by pulsed laser deposition (PLD) from a solid manganin-target (Cu 86 %, Ni 2 % and Mn 12 %). With this method the coating thickness was of ~50 nm. A Q-switched Nd:YAG laser operating on the second harmonic wavelength at 532 nm was used for generation the of micro-plasma. The results indicated that the laser focal conditions and laser pulse energy were important parameters determining lateral resolution, depth resolution and surface sensibility. Three stoichiometric distribution maps of copper, nickel and manganese will be shown. A total area of 5.6 mm x 3.5 mm was sampled with a lateral resolution of 375  $\mu$ m. For quantitative purposes, the data from the coated sample were compared with those obtained from a manganin standard. Significant differences in the distribution of metals on Si substrate were observed.

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# *Posters*

## Effects of Experimental Parameters in LIBS Measurements

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In typical experimental condition, plasma and shock wave dynamics can significantly affect the LIBS signals which, if not correctly considered, can give serious errors in the quantitative determination of sample composition. We report the effect of imperfect focusing and of varying laser repetition rate on the reproducibility of LIBS measurements.

A careful consideration of focusing effects is essential for achieving the high level precision often required in most LIBS applications. Using fast optical and spectroscopic diagnostics we demonstrated that the effect of imperfect focusing can dramatically affect the measured spectral intensities and, in turn, the quantitative determination of material components.

For analyzing the effect of varying laser repetition rate we have studied two different kinds of samples (aluminum alloy and KBr-Cr pressed pallet) using time-resolved spectroscopy and optical and holographic diagnostics. The results obtained allow us to determine that, under typical LIBS operating conditions, the laser repetition rate could greatly affect LIBS measurements on pressed pellets, while its effect is negligible on metallic samples.

In order to study the effect of expanding plasma on LIBS signal, we placed an optical system perpendicularly to the direction of the laser beam and performed a series of LIBS measurements at different times and at various positions of the plasma. The time and space variation of temperature and electron density should be taken into account, since they may influence the accuracy of the results of analytical methods based on the determination of plasma parameters.

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## Effects of Experimental Parameters in Quantitative Analysis of Alloy Steels by Laser Induced Breakdown Spectroscopy

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Laser-induced breakdown spectroscopy (LIBS) has received increased attention as a method for elemental determination in gases, solids, and liquids, due to its high sensitivity, the minimal sample preparation and its simplicity. The method is based on the focusing of a laser pulse on the sample surface and the spectral analysis of the emission of the laser produced plasma. Although the qualitative analysis seems a rather easy task, the quantitative results depend on a number of experimental parameters, which affect the produced plasma. Important analysis parameters include the atmosphere surrounding the sample, the laser pulse characteristics, the sample characteristics and the sampling geometry. In order to achieve reliable quantitative results, these parameters have to be carefully studied, and to be optimized, so the analysis conditions to be kept uniform as possible.

We used a Nd:YAG laser to irradiate the sample, either by 1064nm or 355nm in various intensities, a XY translator as the sample holder, a UV fiber cable for the collection of the emitting light from the plasma and a spectrometer in conjunction with a gated optical multi-channel analyzer (OMA III system) for the analysis of the emission lines. This system allowed both spatially and temporally resolved spectra to be recorded.

The influence of the laser wavelength, its intensity, the temporal evolution of the plasma in air, as well as the sampling geometry were investigated for the quantitative determination of alloy elements with various concentrations in steel samples and calibration curves were extracted for Cr, Ni and Mn in the alloy.

## Elemental Analysis of Aluminum Alloys by Femtosecond Laser-Induced Breakdown Spectroscopy and Time-Resolved Plasma Characterization

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In the last few years, many works have shown a wide range of advantages in the use of ultra-short pulses in laser processing of materials. Due to the short-time scale of the laser-matter processes, there is no interaction of the laser light with the resulting plasma. The laser energy is then fully deposited into the material with a weak thermal diffusion. As demonstrated by recent publications, lower ablation thresholds and a larger efficiency of the material ablation are obtained with high precision and minimal damage. These specific features of ultra-short laser-matter interaction may offer similar advantages in the area of analytical Laser-Induced Breakdown Spectroscopy (LIBS) technique. However, while many studies on LIBS technique have used longer laser pulses (of the order of nanoseconds) on different materials, to our knowledge only a few experiments have been performed with ultra-short pulses.

In this paper, we present LIBS results obtained from aluminum alloy targets at atmospheric pressure, using a Ti:Sapphire laser with pulse duration of 100 fs. For the first time to our knowledge, the temporal behavior of some of the spectral emission lines of a space-integrated aluminum plasma produced by a femtosecond laser is presented. Spectroscopic analysis gave electron density, together with electron and ion temperatures, which were used to discuss the thermal equilibrium (ETL). An optimal temporal window has then been deduced to perform an elemental analysis of aluminum alloy samples. Calibration curves were produced for the aluminum alloying elements, such as magnesium, manganese, copper, iron and silicon. The limits of detection (LOD) for Mg, Mn, Cu, Fe and Si in aluminum alloy are in the order of few ppm (but element-dependent). A comparison of the results obtained by fs pulses with those of ns-pulses will be presented.



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## **Evaluation of Laser Ablation Efficiency as a Function Of Laser Parameters: Comparison Between the Ns, Ps and Fs Regimes**

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The aim of the work was to investigate the influence of the laser characteristics (pulse duration, laser wavelength and intensity) on the efficiency of laser ablation (expressed as the amount of material removed by unit of incident laser energy or fluence) in the conditions of microanalysis (laser spot around 10  $\mu\text{m}$ ). Craters formed in metallic samples were characterized by means of an optical profilometer as a function of the laser fluence for different wavelengths and pulse duration (ns, ps and fs). Each laser beam was characterized in terms of spatial intensity distribution (near gaussian beams) to ensure a valuable comparison of the results obtained in the different experiments.

Results confirm that for high laser intensity, laser-plasma interaction plays a major role in the nanosecond and picosecond regime. In the case of ns pulses, a strong perturbation of the beam intensity distribution at the sample surface, induced by refraction of the beam into the dense plasma, has been observed. It results in a modification of the crater shape. The same phenomena exists in the case of ps pulses but due to a reduced expansion of the plasma during the laser pulse, it leads to a smaller perturbation of the craters diameter. Origin of the phenomena has been confirmed by imaging the plasma expansion during the laser pulse by means of an ICCD camera with 3  $\mu\text{m}$  spatial and 1 ns temporal resolution. According to previous works pointing out the role of inverse bremsstrahlung effect in plasma screening, it has been observed that laser-plasma interaction is enhanced when an IR laser wavelength is used instead of UV.

On the contrary, in the case of femtosecond pulses, no plasma is formed during the laser pulse and laser ablation results from a direct laser-surface interaction. In this case, it has been shown that the ablation efficiency is independent on the laser wavelength and the laser pulse duration in the range of 60 fs – 1 ps as well. This seems to indicate that surface reflectivity of the sample surface does not play a major role in the femtosecond ablation process that is different from the nanosecond one.

For all the tested materials, the best ablation efficiency was obtained for fs laser pulses but it has been founded that the use of a multimode UV ns laser beam focused by a high aperture microscope objective can leads to the same level of performance.

## **15-Fold Enhancing of The Contrast of Libs Excited by Doubled Nd:Yag Laser Pulses**

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The excitation of a plasma on the surface of a target by doubled pulses of a Nd:YAG laser with separation of 15 – 25 us gives rise to an anomalous jump in the intensities of LIBS spectral lines of target elements without noticeable increase in the intensity of the background and emission of atmospheric gases. Such an increase in spectral line intensities and improvement of the sensitivity of spectral analysis, which can be also achieved when one laser is used instead of two lasers, is of fundamental importance for space, airborne and other remote-sensing systems, especially when it is impossible to repeat measurements.

The possibility to control plasma characteristics by an appropriate choice of the parameters of a pair of pulses provides additional advantages over the single-pulse excitation regime with time-domain spectrum resolution LIBS. Specifically, simply varying the interval between the pulses from 20 to 100 ns, we could increase the contrast of spectral lines of the target by a factor greater than ten. Direct interaction of the second pulse with the surface gives rise to an extraction of a considerable amount of the target materials, which can ensure a giant enhancement of the LIBS lines intensity from the proper target and improve the sensitivity of remote analysis. Other advantage is also obviously. Namely, the first pulse cleans the surface from the oxygenized layer and dust in field measurements.

However, the region, where the second pulse of a Nd:YAG laser, which is delayed by 15 – 25 us with respect to the first pulse (such delay times are easily produced with a single laser was used), initiates the breakdown, has not been determined by direct experiments yet. We can observed only that the maximized enhancement of the LIBS contrast (about 15-fold) with double pulses action was achieved with optimized laser beam focal point position over the surface. Its was detuned about (5 – 7)% of the focal length.

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## Study of the Interaction Between a Metallic Plasma Created by Laser Ablation and an Argon Gas at Atmospheric Pressure

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The present study is devoted to the interaction between a metallic plasma produced by laser ablation and an ambient argon gas at atmospheric pressure. The experimental results will be compared to theoretical ones given by numerical simulation.

### Experimental set-up

A Q-switched Nd-YAG laser operates at its fundamental wavelength ( $\lambda = 1.064 \mu\text{m}$ ). It delivers 8 ns FWHM pulses with an energy of 120 mJ, at a rate of 10 Hz. In order to avoid breakdown in the ambient gas surrounding the target, the focus lens is slightly defocused, so the target irradiance is  $10^9 \text{ W.cm}^{-2}$ . A lens collecting the light emitted by the plasma in a direction perpendicular to the incident laser beam gives an image of the plasma (magnitude 4) on an optical fibre (spatial resolution 0.25 mm). This fibre is connected to a monochromator with a focal length of 1.5 m and using a 2400 grooves per mm grating. The detector is an intensified photodiodes array covering a spectral width of 4.5 nm. A PC allows the recording and the treatment of the spectra through a appropriate software. The spectra was obtained by summing 200 consecutive shots. The gate width, for a single shot, is 100 or 200 ns. The targets, used in these experiments, are made of aluminium containing a small amount of impurities homogeneously distributed in its volume and which percentage were known with a good precision.

### Experimental Results

First measurements allow us to determine the metallic plasma parameter by recording some spectral lines of the iron contained in the target. In the spectral range 371-376 nm, the iron spectrum presents eight lines who lead to the metallic plasma temperature determination versus time and space by the use of the Boltzmann plot.

Second ones use the argon 696.5 nm line, corresponding to the 4p-4s transition, to study, spatially and temporally, the argon plasma created by the interaction of argon gas and metallic plasma. As the plasma has a revolution symmetry around a normal axis to the surface of the target, we obtain local values using Abel transform. The intensity and the broadening of this line give information on argon plasma formation kinetics, in particular on the appearance of the diffusion. The latter phenomena follows a period where the mixing between metallic vapour and argon has not yet occurred. After Abel transform, we observe a maximum of the line intensity off the plasma axis. This shows the formation of the argon plasma around the metallic one before complete diffusion.

### Numerical modelling

The hydrodynamic model build in a one 1D uses the continuity equations. The code is based on the control volume method of Patankar. One temperature and mass fraction profiles are needed as initial conditions. A parametric study is made on this two parameters and allows to determine the duration at the end of which the initial profile effects on the plasma properties vanish. For example, until 20  $\mu\text{s}$ , the plasma temperature evolution depends strongly on the initial conditions; it is no more the case later. This shows the fundamental importance of the initial conditions knowledge to perform a valuable modelling of the thermalisation phase of the plasma.

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## Modeling of Plasma LIBS Expansion

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Recently a large interest has been developed to LIBS (laser induced breakdown spectroscopy), a technique which allows measuring concentrations of solid samples, such as soils, metals and alloys [R. Barbini (1999), F.Capitelli (1999)]. In this technique, which consists on the measurements of the emission line intensity of the different species, a laser strikes the sample and produces a plasma, which expands in the atmosphere with the characteristic shape of a plume. The interaction between the laser and the sample produces a plasma, near the surface, which can be described by the assumption of the local thermodynamic equilibrium (LTE). The region far from the surface shows a lower plasma density and temperature, which could produce a deviation from the equilibrium state. Recently Capitelli et al. [M. Capitelli (2000)] developed a model to verify the existence of LTE conditions in LIBS plasmas.

In this work we want to simulate the expansion of the plume produced after laser-matter interaction, in the assumption of LTE. In previous works [R.Kelly (1992)], evaporated material is considered chemically inert and therefore the composition of the plume is considered constant. In this work we introduce the study of thermodynamic equilibrium in the plasma. This approach allows to calculate equilibrium composition and thermodynamic properties of the different species, which are present in the plume. So, it is necessary to coupling a fluidodynamic model, which describes the plume expansion, with a thermodynamic model, to calculate thermodynamic properties and equilibrium composition.

In particular, the plume expansion has been studied via fluid dynamic equations (Euler equations) along the plume axis. In each point of the plume expansion we suppose a local thermodynamic equilibrium. Therefore the composition can be calculated by means of fundamental concepts of statistical thermodynamic, from partition functions of different species. After the partition functions, it is possible to determine equilibrium constants and therefore the equilibrium composition of the considered mixture [D. Giordano et al.(1994)].

The problem is limited to the calculation of equilibrium composition and thermodynamic functions in any position of the plume expansion, neglecting diffusive processes (viscosity, diffusion, thermal conductivity and so on). If speed of reactions is comparable with flow characteristic time a chemical kinetic approach should be used. The usual theoretical approach to the fluid dynamic plume expansion consists on the analytical solution of Euler equations, which requires strong approximations and the use of empirical data.

In this paper we present a numerical model to solve the plume expansion equations (Euler or Boltzmann), calculating the time evolution of temperature, pressure, density, composition profile [P. Comte (1993)]. To confirm the validity of our theoretical approach and to have information about the existence of LTE or non equilibrium, we can simulate the emission spectra of different species, which are present in the plasma produced during laser-matter interaction, and we can compare our results with experimental results.

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## Effects of Oxygen Concentration on Laser-Induced Breakdown Spectroscopy Measurements of Toxic Metals

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Laser-Induced Breakdown Spectroscopy (LIBS) has been considered for some time as a potential continuous emissions monitoring method for toxic metals from thermal processes. (Hahn 1997, Buckley 2000) Recent results indicate the possibility that longer delay / gate combinations may significantly enhance detection limits for many species, including detection limits for several of the toxic metals. (Hahn et al., in preparation) This paper discusses the effect of oxygen concentration on the detection limits of Pb, Cr, Cd, Be, and As.

LIBS measurements of single-component aerosols in N<sub>2</sub> / air mixtures were made with a ¼ meter spectrometer coupled to a time-gated intensified CCD camera. For some species the effect is significant; for example, the effect of O<sub>2</sub> on Pb is nearly a 2.5% drop in signal for every increase of 1% in mole fraction of O<sub>2</sub>. In contrast, for other species such as Be, the effect is negligible. This effect is not observed at shorter delay times following the plasma formation. We discuss the mechanism(s) believed to be responsible for the observations, and the potential ramifications of these findings for measurements in gas streams with varying O<sub>2</sub> concentrations, such as combustion effluent streams.

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## Dispersion Relations in Weakly Degenerate Plasmas

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From a Quantum Mechanical point of view, electrons in laser produced plasmas can be regarded as weakly degenerate. For instance, for a plasma with electron density of  $10^{22} \text{ cm}^{-3}$  and electron temperature of 1 eV, Sommerfeld's parameter is approximately 2. Under these conditions, the usual dispersion relations for waves in plasmas need to be corrected to account for degeneracy. In the present work, starting from the transport equation with a simplified version of the BUU collision kernel and taking into appropriate account the self-consistent electric field, the propagation of waves impinging on a plasma with weakly degenerate electrons is investigated, and dispersion relations accounting for degeneracy are derived.

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## Characterizing the Effects of Sample Composition on Plasma Shielding in LIBS Analysis

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### Introduction

Plasma shielding is often invoked as a source of non-linear performance in laser ablation (LA) techniques used for material removal, material processing and chemical analysis. Sample composition including the chemical form of the analyte has been found to have profound influence on elemental response factors in LIBS and LA sampling for ICP analysis (Montelica-Heino *et al.* (1999)). To determine the extent of plasma shielding and the degree to which sample composition and physical characteristics influence plasma shielding in LIBS, we performed plasma transmission measurements (Mao and Russo (1997)) on compacted powder samples of varying composition.

### Experimental

Samples were prepared by mixing different analytes at different concentrations in cellulose or lactose matrices and compacting these mixtures into thin (1 mm) disc shaped samples. These were analyzed by LIBS using a Nd:YAG laser operated at the fundamental wavelength (1064 nm). The samples were sufficiently thin that the diffuse transmitted radiation could be measured using a fast photodiode placed below the sample and coupled to high-speed high-bandwidth digital oscilloscope. By assuming the rising profile of the incident and transmitted light are the same (i.e. assuming shielding is minimal very early in the laser pulse), the profiles can be compared and a transmitted fraction of laser energy can be determined. LIBS emission measurements were obtained for the same samples and attempts were made to establish a link between the plasma transmission (shielding) and emission intensities.

### Results

Preliminary results show that plasma shielding is significant at the energy levels needed to obtain sufficient emission intensity and occurs within 1 ns of the beginning of the laser pulse (7 ns duration). The extent of plasma shielding depends on sample composition. For example, for MgO in cellulose or lactose matrices shielding increased with the increasing concentration. In particular, the degree of shielding increases substantially between the blank and first concentration (0.5%). The emission intensity response factor varies as a function of concentration and the change can be linked to changes in the degree of shielding.

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## **Formation of Switching Waves in Optical Bistability Scheme based on Dependence of Absorption Coefficient of Semiconductor on electric Field**

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We consider the action of laser pulse of the picosecond duration on a semiconductor. Laser pulse creates non-equilibrium distribution of electron-hole plasma that is created due to a generation of electrons from donor levels. As consequence of this, electric field is generated. The field changes an absorption coefficient of semiconductor. There are two physical mechanisms of absorption coefficient variation. First of them appears due to re-normalization of gap. The second mechanism appears due to a tunnel effect: electron riches a conductivity zone from donor level under the action of high electric field strength. It should be noticed that we take into account also the dependence of electron mobility on electric field.

To make a computer simulation, one will be create a conservative difference scheme. It should be emphasized that computer simulation requires a great accuracy. Hence, a derivative of electric field potential with respect to spatial coordinate is calculated with the help of the fast Fourier transformation. Only in this case a required accuracy achieves.

Among the results obtained from computer simulation, one can be mentioned a development of localized structure with a high electric field strength. This structure appears under certain conditions on a donor concentration and on a dimensionless coefficient of electron diffusion. It is important that for its formation, the dependence of electron mobility from electric field must be negligible. The domains of structure displacement near the moving boundaries of domain of generated free electrons. In time, a speed of boundary motion decreases and the difference between concentrations of free electrons and ionized donors takes place in decreasing domain too. As a result, electric field strength increases and the dimension of structure decreases.

The localized electric field can induce a tunnel transition of electron from valance zone to the conductivity zone in this domain. Then, if the transition from conductivity zone to the valance zone is a radiative one, a new spectral component appears after the recombination electron to valance zone. Other spectral components correspond to electron recombination with ionized donors. Those components are close to the frequency of propagating laser radiation. It may be expected that intensity of the new spectral component will depend on electric field strength. Such a way, we can estimate electric field strength. Using this effect, we can show a motion of electric field domain and switching wave in real time.

If the dependence of electron mobility from electric field takes place, one can be appeared a formation of switching waves. They are due to a realization of optical bistability based on the dependence of absorption of semiconductor on electric field potential.

In conclusion it is necessary to emphasize that using the mentioned above mechanisms of absorption of laser radiation there is a possibility of creation of optical bistability element with high speed of switching belong to pico- or femtosecond time interval.

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## Spectroscopic Characterisation of LIB in Liquids, Solids and Gas Samples for Quantitative Determination of Traces

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Laser Induced Breakdown Spectroscopy has received increasing attention due to its advantages in simplicity and versatility. It is a good semi-quantitative technique for in-situ determinations and has been used with success in different types of applications. One of the major drawbacks of the technique has been the difficulty in obtaining accurate quantitative results. In this respect the most convenient approach for quantitative analysis, is to determine elemental abundance comparing trace lines signals with intensities obtained from predetermined calibration curves made with standards [L. J. Radziemski, et al. 1983-Cremers, 1987-B.C. Castle, et al, 1997- R.L. Vander Wal et al, 1999]. However, it is not always possible to obtain such curves, either because there is no chance to make the experiments, or because there are no available standards. An alternative method, although more arduous, is to analyse the basic Physics of the plasma processes and to use the equilibrium relations, i.e. Boltzmann distribution and Saha equation, amongst the atomic levels involved and the electron density and temperature of the plasma [Ciucci et al, 1999]. Experimentally the crucial point is to obtain both equilibrium and thin plasma conditions in order to apply the aforementioned conditions. In our LIBS experiments, the signals were usually small and depending of the experimental situation, the lines observed were self-absorbed in the optically thick plasmas. Also, we not detect usually too many transitions of the element under study. Thence, to make a Boltzmann plot in these conditions introduces errors in the Temperature determination.

We hereby report results of LIBS experiments on liquids, and solid targets, using the addition of a known concentration of an element to the sample, which is used in the laser generated plasma characterisation. The detection system allows the temporal discrimination of the detected spectral emission to which the background is conveniently subtracted. The analysis then proceeds to identify the temporal intervals at which equilibrium and thin plasma conditions are nearly fulfilled. Those time intervals vary according to the experimental situations and the sample under analysis.

We present the determination of the concentration of Li in an Al-based alloy, the detection of trace concentration in an aqueous solution at atmospheric pressure, and the determination of Pb in oil-based propellants.

In the first example, the sample was enclosed in a Xe environment, in order to use Xe transitions as the plasma characterisation element. The Li concentration was determined in the range 30-40 ppm/wt. In the second case, a sample of tap water was doped by a known concentration of Be (50ppm) which was used as the plasma characterisation element. In the last example, the same element was used as the examination contaminant.

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## Laser Induced Breakdown Spectroscopy For Semi-Quantitative Elemental Analysis in Soils and Marine Sediments

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The Laser Induced Breakdown Spectroscopy (LIBS) technique was applied for elemental concentration measurements of soil and marine sediments.

A compact instrument, suitable to both laboratory and field operation, has been designed and tested. Initial sample preparation is not required. An appropriate software for semi-quantitative analysis of both metal and non-metal elements, as for example Barium, Calcium, Silicon etc., has been developed.

Analytical method includes plasma modelling referring to temperature and electron density, as well as spectra normalisation in order to reduce matrix effect and influence of laser parameters on quantitative measurements. The computational algorithm takes into account only atomic species and their first ionisation states, that has been demonstrated sufficient in our working conditions where plasma temperature is typically between 7000 K and 9000 K. All line intensity calculations are referred to the lines previously fitted by Voigt profile, and only emission lines free of overlap with other not very weak lines, were considered in plasma modelling and quantitative analyses.

Initially, calibration curves had been generated for each element of interest, basing on certified samples from different provenience and matrix composition, and inserted into data base considered specific for given experimental layout. Consequently, the concentration of one element from unknown sample can be determined directly, without analysing complete matrix composition.

The LIBS method here developed was tested on a priori unknown samples, and resulted in error of concentration measurement varying from 20% to 40 %, over concentration range covering few orders of magnitude. The measuring error depends on element type as well as concentration range and number of certified samples for given element that had been used for initial calibration.

From different testing on the same samples, the calculated element concentrations result independent on energy fluence at the sample surface as far as it is sufficient for plasma generation and the conditions of Local Thermal Equilibrium (LTE) are maintained through appropriate choice of temporal window for signal acquisition.

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## Comparative Analysis of Ca using LIBS and Standard Techniques in a Depth Soil Profile

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The use of Laser Induced Breakdown Spectroscopy (LIBS) in soil analysis has been extensively studied in the last years as a method for in situ detection of hazardous metals [1]. One of the principal problems of LIBS arises from the influence of the matrix composition and the need of calibration curve, even though much progress has been made lately [2]. On the other hand, soil contains different compounds with the same cation, some of which are soluble either in water or in acid that can be easily determined with standard techniques. Other kind of compounds, such as silicates are not soluble and need an extra treatment which implies the use of melting compounds and high temperature oven.

In this work we present a method based on LIBS technique that allows to us determinate the concentration of total  $\text{Ca}^{2+}$  in soil. The line intensity ratio of the emission of  $[\text{Ca}^{2+} / \text{Ba}^{2+}]$  in a  $\text{BaCl}_2$  matrix was measured in order to obtain a calibration curve [3]. This result was then used to determine the in-depth concentration profile of Ca in a soil of Patagonia, from the surface to 18 m. The samples were also analyzed using standard techniques in order to compare the results with those obtain by LIBS. The advantage and the disadvantage of the method are discussed.

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## Application of LIBS Technique to Environmental Diagnostics

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The calibration free LIBS method developed and patented at the IFAM-CNR laboratory of Pisa allows for a fast and accurate multi-elemental analysis of materials without any preparation of the sample.

The detection limits for the elemental traces are generally of the order of ppm.

We have applied this technique on the following certified samples: Pacs-1 (Marine sediment), GBW07310 (Stream sediment), GBW07403 (Soil), BCR176 (City waste incineration ash), NIST1575 (Pine), BCR62 (Olive leaves), BCR482 (Lichen), BCR184 (Bovine muscle), Dorm-1 (Dogfish muscle).

At the same time these samples have been analyzed at the Istituto di Ricerca Centro Studi Ambientali of Rimini with a spectrophotometric technique of atomic absorption and with an Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES).

The results obtained from the comparison of the two techniques are in a good agreement for all the samples, thus demonstrating that a further development and implementation of the CF-LIBS technique for environmental analysis is possible and important.

Such a technique is in fact particularly suitable for this purpose because of its intrinsic fastness, the possibility of 'in situ' measurements and the accuracy of results.

## Trace Analysis of Alloy and Rock Sample by Using Laser-Induced Breakdown Spectroscopy

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The porphyry sample and zircalloy were analyzed by using laser-induced breakdown spectroscopy (LIBS). The third harmonic of the Nd:YAG laser, 355 nm, was used as an ablation source, while the emission signal was detected and analyzed by using a Spectra pro-500 (Acton) spectrometer with ICCD detectors. The porphyry has been known to generate far Infrared emission that is assumed to play important role for the human health. In addition recent application of the porphyry includes such fields as ceramic industry, processing of the industrial waste, preserving the agricultural products, etc. It can be also used as a replacement of the pesticide in agricultural industries. These many applications of the porphyry may have something to do with the minerals contained in the sample. The porphyry is known to have Si, Al, Fe, K, Na, Ca, Mg as major composition. Ti and Radium also known to be present in porphyry in a trace level. We have investigated the composition of the Korean porphyry. Meanwhile, the zircalloy is an important alloy in nuclear industry. The analysis of the trace elements contained in the Zircalloy may provide informations in developing zirconium alloy with better characteristics.

Fig. 1 is the typical emission spectra of the porphyry, The prominent emission lines are identified as representing Ca, Al, Si, Fe. But in spectra obtained in other wavelength range, other elements such as Hg, Mg and Sr that are not identified in the previous study were identified according to the assignment done in the present study.

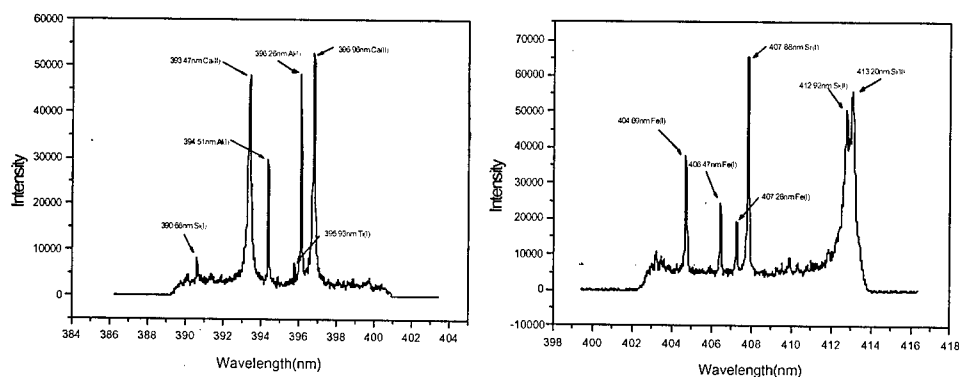


Fig. 1. LIBS spectra of porphyry sample. The laser energy was 20 mJ/pulse, and the buffer gas was helium.

## Qualitative and Semi-Quantitative Characterizations of Mineralous by Libs Technique

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The accomplishment of sampling campaigns and mineralogical mapping are of vital importance for mineralogy and geology. In this work, the viability of the use of the LIBS (Laser-Induced Breakdown Spectroscopy) technique for fast qualitative and semi-quantitative mineral samples characterization is checked. As an example, it was studied samples of ores, not powdered and not homogenized, as well as kaolin samples in its natural composition.

The results obtained by LIBS technique are compared with other techniques: scan electronic microscopy, EDS and chemical analysis. The results are satisfactory. In the case of kaolin and ore samples, it was possible to detect, qualitatively and semi-quantitatively, the presence of the more important chemical elements of their compositions (*Al*, *Si*, *Ca*, *O*, *Fe* and *Ti*). These results were compared with the values of its correspondent oxides concentration. The principal contaminant elements of the commercial kaolin are iron and titanium. In order to obtain better quality of its products, it is important to determine the distribution of the iron in the kaolin used in the paper industry. The low intensity of the Fe lines had not allowed the construction of a curve for a quantitative evaluation of Fe in kaolin samples. In spite of that, the use of this technique is viable for Fe detection.

Correlation curves of the intensities of the spectral lines of the principal elements that compose the samples with the data obtained by conventional techniques are presented.

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## Chemostratigraphy - The Elemental Solution using LIBS-OES

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Chemostratigraphy is a geological technique that aids the correlation of sedimentary rock sequences, with the ultimate aims of finding new oil and gas fields and increasing the productivity of existing fields. The technique is based on the recognition of changes in the bulk inorganic geochemistry within sequences of sedimentary rocks and often sequences of seemingly homogeneous rocks can be divided and correlated between oil wells using chemostratigraphy. Current analytical methodologies are based on Inductively-Coupled Plasma (ICP) technology. As successful ICP analyses require extensive sample preparation, which increases both time and cost, and a clean laboratory environment, field-based studies and very large-scale studies are often precluded because of cost and time restrictions. To decrease the time and cost involved in the acquisition of geochemical data from rocks an alternative analytical option is required. Halliburton Energy Services sponsored Chemostrat Consultants to investigate the potential of the commercially available LIBS-based instrument (Tracer<sup>TM</sup> 2100) manufactured by APTI Inc.

During the development program new methodologies have been established that enable rock samples to be prepared in less than 5 minutes. In addition, refined analytical protocols have demonstrated the ability of the instrument to determine, with good accuracy and precision (2-3%), the concentrations of nine major elements (Si, Ti, Al, Fe, Mg, Mn, Ca, Na and K) and nine trace elements (Ba, Cr, Cu, Li, Ni, Sr, V, Zn and Zr) in wide range of rock types including sandstones, shales, limestones, bauxites, granites and basalts. Using certificated rocks standards calibrations of  $>0.98R^2$  can be achieved on all major and high abundance trace elements with excellent dynamic range such as 0.1%- 50% for  $Al_2O_3$ , and 0.1-50% for CaO and 3-1500 ppm for Zr. To compare the Tracer<sup>TM</sup> data with ICP-AES data, samples from Triassic sequences in North Africa have been analysed by both techniques. Overall there a strong correlation between the Tracer<sup>TM</sup> geochemical data and those derived from ICP-AES. This test demonstrates the potential for LIBS-OES as alternative analytical instrument to ICP-AES. However, Tracer<sup>TM</sup> also has additional benefits over ICP. The instrument requires minimal sample preparation and is a desktop, self-contained unit that requires no specialized laboratory support and yields rapid, real time elemental data in seconds. By using this instrument, a new chemostratigraphic service has been established by Halliburton Energy Services and Chemostrat Consultants called LASERSTRAT<sup>TM</sup>, which involves the acquisition of geochemical data on an oil rig during drilling operations as well as in laboratory for large-scale projects that have rapid turnaround times.

## **Interaction of Pulsed Laser with Ionic Solutions. Applications to Water Salinity Measurement**

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The salinity of water solutions has been measured by the LIBS technique using the second harmonic of a pulsed NdYAG laser at 532 nm. The laser beam is focused on the surface of the solution or in an aerosol formed from a solution, and emission from sodium atoms and ions is recorded with temporal discrimination with a 0.6 m focus monochromator. A second laser pulse issued from a dye laser allows the observation of diffusion by the plasma after a variable delay. By varying some parameters – concentrations of solutions, laser energy, delay of observation – some conclusions have been reached about the processus of formation of the excited species in the plasma, involving recombination ion-electron and cascading.

Saturation effects appear in the case of surface interaction: self absorption for Na emission, which is known to be strong, is proved not to be the main phenomena at the origin of this observation, as no saturation is observed with aerosol interaction, where linearity of the signal intensity with concentration is obtained. Data with magnesium, and calcium solutions confirm that cascading processes follow ionic recombination to explain the main features of the observations made on sodium emission.

We propose the application of this technique to monitor *in situ* and in real time the water salinity, including Ca and Mg concentrations measurement, which are not available by standard conductivity methods, in a portable instrument.



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## LIBS Technique for The Diagnostic of Pollutants in Water

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Plasma diagnostic achieved by a study of the Stark profile is a commonly used technique in plasma physics and the physics of the stellar atmospheres (1,2,3)

We have extended this method to diagnostic by LIBS technique (4), the plasma induced by pulsed laser (YAG,  $\lambda=532\text{nm}$ , 10ns, 10-40 mJ) in interaction with  $\text{CaCl}_2$  diluted in water at different concentrations.

Spectral lines are strong and have extended collisional wings due to the interaction with electrons, and ionized atoms and then Stark broadening is important.

For that cases where line shapes are dominated by Stark broadening a common and widely used model consists in using an impact approximation for the electronic broadening and a statistic approximation for the ionic component (5).

In this communication we present:

Results of the experimental spectral line width  $\Delta\omega$  and shift  $\delta$  of the doublet of ionized calcium atom  $\text{Ca}^+$

$\lambda=3934.77 \text{ \AA}$  and  $\lambda=3969.59 \text{ \AA}$

Calculation of these parameters  $\Delta\omega$  and  $\delta$  based on the impact and quasi-static theory and semi classical approximation

The comparison of these results which leads to an electronic density  $N_e=$

$10^{18}\text{cm}^{-3}$ .

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## **On-Line Characterization of Recycled Thermoplasts from Consumer Electronics by Laser-Induced Plasma Spectroscopy (LIPS)**

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Modern polymers contain a wide variety of additives to adapt their properties and to fulfill legal regulations. Many of these additives comprise several inorganic components: pigments to adapt the colour (e.g.  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{Fe}_2\text{O}_3$ , and soot), flame retardants to improve the safety (e.g.  $\text{Sb}_2\text{O}_3$  combined with brominated organics), and various stabilizers (e.g. organic compounds of Ba, Sn, and Zn). The mass fractions of these additives can cover ranges from a few ppm to several percentages. Together with the extended use of polymers the amount of domestic and industrial waste has increased and also the need for efficient recycling systems. An important part of a profitable recycling system for thermoplasts (especially from consumer electronics with lifetimes of 1-2 years) is an on-line analytical method for instant characterization or separation of plastic fractions during the recycling process. The aim of this project is to apply laser-induced plasma spectroscopy (LIPS) for multielemental process analysis of recycled thermoplasts from consumer electronics. Via LIPS the metal content of the recycled compounds can be monitored on-line which is important for the quality assurance of the recyclates and to meet the requirements of legal limit values for toxicological relevant metals like Cd, Cr, and Pb.

A prototype of a LIPS system, based on a frequency-quadrupled Nd:YAG laser and an Echelle spectrometer, was developed for laboratory measurements and on-line analysis on recycling plants. Multielemental analysis is possible with an Echelle spectrometer that provides high resolution over the range of 200-780 nm. The data are instantly available in digital form and can be included into the process control to allow an exclusion of contaminated fractions. Within this project, a sample lot of 100 samples of plastic scrap from electronic applications was analyzed for metal components metals (Ti, Sb, Zn, Sn, Cd, Cr, Pb, Al, Mg, Si, Ca, Ba) of additives such as flame retardants, pigments, stabilizers and fillers. For the more frequent components Ti, Sb, Zn, Sn, and Cd linear calibration plots with satisfactory limits of detection (50-500 ppm) were obtained. The use of multivariate calibration models improved the analytical figures of merit considerably. Reference analysis was performed by dissolution of the samples in suitable organic solvents and TXRF analysis (a new procedure for which validation was ensured by INAA analysis). In addition, results from a test campaign, where the method was applied for the real-time monitoring of the metal content during the extrusion of recycled material in a double-chain extruder within a recycling plant.

## Characterization of Encrustation on Pentelic Marble with LIBS

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Encrustation was formed on exposed marble, as a result of physico-chemical processes occurring between the stone surface and atmospheric pollutants (Gauri and Holdren, 1981). The encrustation of marble, according to its different morphological characteristics and chemical composition was classified, as follows: i) black crusts, ranging in thickness between 20  $\mu\text{m}$  and several mm, consisting of gypsum, black particles, iron oxides, soot, residual calcite, mica flakes, quartz and numerous organic constituents in low concentration; ii) crusts (up to 1 mm of thickness) originating from deposition of soil-dust on the stone surface, which were observed on stone artworks excavated or located amongst ruins and consist mainly of silicate minerals, gypsum and calcite; iii) biological crusts, which are formed from the colonization of different classes of organisms and micro-organisms. In particular, black crusts were divided into two groups: the first is the thick dark encrustation also called dendritic (tree-like) with a thickness up to 2 mm, and the second is the thin compact dark encrustation with a thickness up to 0.2 mm.

In order to minimize damaging effects of the conservation treatments a physico-chemical characterization of the encrustation is required. The majority of the employed analytical techniques for the material characterization are destructive and cannot be performed in-situ.

In this study Laser Induced Breakdown Spectroscopy (LIBS) has been performed to carry out a qualitative elemental and semi-quantitative analysis of black and soil-dust encrustation on Pentelic marble during the laser cleaning with KrF and XeCl excimer lasers. Furthermore, LIBS has also been performed for the characterization of the orange-brown monochromatic layers from the Athens Acropolis monuments. Emission spectra of the encrustation in the spectral ranges 240-310 nm, 310-380 nm, 380-630 nm and 580-900 nm were obtained. In the spectral range from 240 to 380 nm Fe, Si, Al and Ti were detected originated from the atmospheric pollution, since these elements are absent in the emission spectrum of marble.

In the dendritic black crusts the concentration of Si, Al and Fe decreases remarkably after 10 laser pulses, which correspond to a layer removal of 100  $\mu\text{m}$ . The thin black crusts show a gradual decrease of the concentration of these elements from the second up to the sixth laser pulse. The emission spectrum of the seventh laser pulse, which corresponds to a depth of 60  $\mu\text{m}$ , resembles the spectrum of the pure marble. In soil-dust crusts Fe, Si and Al disappear after the fifteenth laser pulse, which corresponds to a depth of 350  $\mu\text{m}$ .

The analysis of the monochromatic layers of Parthenon shows that Fe, Si and Al gradually decrease during the first laser pulses. Afterwards, these elements and up to the twenty-fifth laser pulse show remarkably higher concentrations, suggesting that they mainly originate from other sources than the atmospheric deposition. This finding is consistent with the notion that conservation treatments performed in the past led to the enrichment of Fe, Si and Al in the monochromatic layers (Frantzini et al., 1984).

The characterization of encrustation performed with LIBS is in accordance with the results of SEM-EDX and the thin section study. Therefore, the LIBS technique provides information both on the composition and thickness of the encrustation. LIBS can also be performed in-situ and is considered as a quasi-non destructive technique for the analysis of exposed marble artefacts.

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## **High quality laser cleaning by laser parameters control: expected improvements by on line diagnostics.**

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Laser cleaning procedures have demonstrated excellent results in the conservation of cultural heritage. The selection of suitable laser wavelength and irradiation parameters allow an extremely controlled ablation process for the removal of degraded superficial layers in various materials.

Nd:YAG lasers have been successfully employed in the cleaning phase of historical buildings and valuable statuary from dark sulphation crusts. Erbium and excimer lasers have found their application in the cleaning of darkened organic layers on paintings, paper and parchment. Infrared lasers have been employed with metals in order to take advantage from the general low optical absorption.

In many cases the selection of suitable wavelength and pulse duration turn out to be the key features to achieve almost negligible release of heat or mechanical forces inside the material substrate. Our proposal of a short free running Nd:YAG laser operating at 20 ns pulse duration is an example of a specifically designed laser system, to avoid the problems of plasma generation with high power Q-switch regime, or the problems of material melting with too long free running pulses.

In conclusion at IEQ we are pursuing on the basis of suitable laser parameters the achievement of high quality in the cleaning procedures. With these criteria we have demonstrated results of excellence on stones and metals by means of intrinsic properties of the laser process.

In the same time several optical diagnostic techniques have been developed up to a level of practical use in on line monitoring of the laser process. LIBS and Raman spectroscopy appear so far more suitable in this respect. Several authors have demonstrated their importance for qualitative and quantitative recognition of the material composition and provenience, for pigments, binders, varnishes and so forth. Their association to a laser cleaning procedure, as an on line source of information on the composition of the irradiated volume, will provide important informations about the stratigraphy of the complete surface under irradiation which otherwise could be achieved only by spot sampling.

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## Characterization of Red Lakes in Old Paintings

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Lakes have been largely used since antiquity as dyes in textiles and pigments in paintings. Lakes are made by an organic dye, or a mixture, and an inert support like aluminum hydroxide. Red lakes, namely Madder, Cochineal, Kermes and Lac lake, are the most important and generally used. In general, the analysis of old paint samples encounters two problems: first, the amount of sample available is always very small, and secondly, the chemical composition has a high degree of complexity. Thus, the identification of lake pigments in paintings is linked to the possibility of adopting an analytical procedure able to detect anthraquinonic compounds at very low concentrations present in a matrix constituted by inert support and organic binder media.

In the present work an analytical procedure for the characterization of red lakes is described. This procedure includes the use of three analytical instruments. Laser Induced Plasma Spectroscopy, Electrothermal Atomic Absorption Spectrometry and Liquid Chromatography with spectrofluorimetric and spectrophotometric detection. Laser Induced Plasma Spectroscopy and Atomic Absorption Spectrometry are proposed for the identification of the inert support used in lake preparation: the first one allows the elemental characterization at ppm detection level directly on the solid sample, and the second one is used for further identification of metals in the hydrolyzed sample solution used for the chromatographic analysis of organic dyes. The main organic constituents of lakes (namely alizarin, purpurin, carminic acid, laccaic acids, kermesic and flavokermesic acids) are separated on a C18 chromatographic column and quantified by UV-VIS and fluorescence detection at picomole levels. The results obtained with the three analytical techniques on the same sample give sound and reliable information on the pigments used in the painting.

The analytical procedure was tested and validated with pure lakes prepared according to old recipes and reference samples prepared at the Opificio delle Pietre Dure of Florence (Italian Ministry of Cultural Heritage - Italy). Finally, results relative to samples from Macedonian tombs (Antemio and Ainea) dated from II-III sec. B.C. are discussed.

## **LIBS and Hyper-spectral Imaging Analysis of Pigments on Illuminated Manuscripts**

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Laser Induced Breakdown Spectroscopy (LIBS) was used for the first time in the identification of pigments in an illuminated manuscript. The manuscript is part of an old ecclesiastical book made on parchment. The analysis focused mainly on the pigments on an illuminated initial letter "T" and on the gold and red paint used in several parts of the writing. In view of the fragility and sensitivity of the manuscript and the fine structure of the writing, the LIBS analysis was very delicate and demanding. For this reason careful optimisation of the irradiation and detection parameters was done beforehand by using model samples. This led to the successful analysis of the pigments in a practically non-destructive way as verified by optical microscopy performed before and after the LIBS measurements.

In parallel to the LIBS analysis, hyper-spectral imaging techniques were used in the examination of the manuscript, which enabled the mapping of the pigments' spatial distribution on the illuminated manuscript on the basis of their characteristic ultraviolet, visible and near infrared absorption spectral features.

Identification of pigments and inks is of great importance for the dating and systematic characterisation of illuminated manuscripts and, as shown in this work, a combined analytical approach can provide with very interesting and useful information.

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## Surface Compositional Mapping of Pigments on a Roman Fresco by CF-LIBS

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Laser Induced Breakdown Spectroscopy is a technique particularly suited for surface compositional mapping, because of the intrinsic speed of analysis, which allows for a fast sampling of relatively large areas in few seconds. However, the large amount of spectra accumulated asks for automated analysis of the experimental data.

In this paper, results are reported on the first application of CF-LIBS technique to quantitative compositional surface mapping. A sample from a roman fresco (St. Albans, UK - II century AD) has been analysed on a 11x11 square mesh, covering about 0.2 cm<sup>2</sup> of its surface. The 121 resulting spectra, acquired with an Echelle spectrometer, all span in a single shot the whole NUV-NIR range from 200 to 800 nm. This set of spectra was analysed with LIPS++<sup>TM</sup>, a specialised software for LIBS spectral analysis developed at IFAM, which implements the CF-LIBS and automatically performs all the operations on the spectra needed for the application of the CF-LIBS algorithm.

In this way, a quantitative compositional mapping of the principal components of the fresco pigments can be obtained automatically, in few minutes. The experimental results show a very good correlation with the visual appearance of the sample, with a marked increase of Ca contents, coming from the plaster under the fresco surface, in the zones where the pigment is damaged or missing, and a corresponding decrease of the main pigment components (mainly Fe, Cu and Al) in the same zones.



Fig.1 – Detail of the region of the roman fresco investigated by CF-LIBS

## Analysis of Lead Coins by Time Resolved Laser Induced Breakdown Spectroscopy

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Time REsolved Laser Induced Breakdown Spectroscopy method (TRELIBS) has been developed at the Centre d'Etudes du Bouchet (CEB), in France, to answer to real necessity of sensitivity and selectivity in detection of gases or polluted surfaces. Focusing powerful laser pulse on a surface produces the vaporization of small amount of the sample, then induces, near the focal region of the lens, high temperature plasma. By using spectral and time resolved plasma emissions, the elemental composition of the material can be determined.

The military applications of TRELIBS are the real time detection and the identification of biological and chemical agents with analysis of polluted surfaces. Another purpose of the analysis has been developed : the study of archaeological materials, like lead coins belonging to the museum of Picardie (Amiens, France). Thanks to the determination of elementary composition, we can establish conservation conditions to prevent or stabilize the lead coins corrosion.

The main advantage of this method is that, without laborious chemical preparation, it especially provides direct analysis of solids. The optical access to the sample is required only, and sample contamination-induced risks are minimal. The LIBS technique is very promising for archaeological material. There is no problem with the sample dimension, or the surface appearance, nor the chemical or physical proprieties and, it's a qualitative analysis in real time of all atomic elements (contrary to X-ray fluorescence). Another advantage is that this technique can be adapted to corroded coins without cleaning them. The volume of impact is very small: diameter is inferior to 100  $\mu\text{m}$  and the depth is around 30 nm. As this method is really rapid, it's possible to carry out many analysis in the same conditions, with a better reproducibility.

The first qualitative analysis has been achieved in comparison with X-ray fluorescence, and the results have shown that LIBS technique is really adapted to this sort of objects. Indeed, in opposition to X-ray fluorescence which is a global method, the LIBS technique is more selective and allows to analyze superficial details and to characterize the patina and the metal. The choice of several spectral windows gives the profile of the coin composition and avoids potential problems of interfering atoms. The shot repetition at the same location permits to analyze the metallic zone under the patina. It gives the composition evolution in function of the depth, and it points out the heterogeneity in the material. Besides, as all elements are detectable, we can determinate the light atoms which are attribute to pollution on the coins. Finally, as the limits of detection are low, LIBS method has shown that some coins contain silver and bismuth.

Our goal is now to establish a miniaturization project for the in-situ analysis in military and civilian applications, to reach lower thresholds requested because of the high toxicity of CW agents and to have a minimal impact in archaeological objects with a good sensitivity.



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## **LIPS analysis of bronze artifacts: Ghiberti's "Paradise Gates" and Verrocchio's "Christ and Doubting Thomas"**

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Lorenzo Ghiberti (1378-1455) was one of the most important sculptors and Andrea del Verrocchio (1435-1488), Leonardo's "maestro", was one of the most skilled founder of the Renaissance in Florence. In the present study some bronze specimens coming from two important bronze Renaissance artifacts, Ghiberti's east door (Paradise Gates) in the Baptistery of Florence and Verrocchio's St. Thomas in Or San Michele, have been analyzed by means of LIPS and other techniques in order to point out the differences in the composition of the alloys.

This study was aimed to validate the LIPS results against more consolidated analytic techniques (ICP, EPMA, AAS, PIXE and SEM) in view of a more extensive study addressed to the solution of some problems still open, such as the possibility of deciphering the "bottega" and the relative casting technique, the connection between the plasticity of the artifact and its shape and eventually the dependence of the use of some alloying components on the fortune of the client.

In particular, the comparison between SEM and LIPS results coming from the present study, confirms once more the latter's validity for bulk analyses of bronze artifacts. In particular, in Table I are reported the values for the major alloying components for the Door of Paradise, which evidence a good agreement between SEM and LIPS results, with a marginal discrepancy only for the Zn-content, which may be explained considering that the most reliable and intense Zn lines are emitted in a spectral region characterized by a poor detection efficiency of the LIPS setup used in this study.

Table I: Major alloying components for the Door of Paradise: SEM and LIPS analyses

	Cu%	Sn%	Pb%	Zn%
SEM	95	2.7	0.9	1.4
LIPS	93.4	2.1	1.4	3.0

The data obtained in the present work particularly highlight the complementarity of the two used techniques: with the LIPS procedure, in fact, it is possible to obtain compositional information with no sampling, on the other hand, the SEM analysis, allowing to obtain the image and the map distribution of the different elements, enables the metallographic investigation which can evidence the working procedures used by the artist.

Moreover, the possible use of LIPS for depth-profile analysis may increase the efficiency of the complementary use of the two techniques in order to obtain more complete information also about the composition of the patinas.

## Analysis of Stained-Glass Windows by Time Resolved Laser Induced Breakdown Spectroscopy

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Time Resolved Laser Induced Breakdown Spectroscopy method (TRELIBS) has been developed at the Centre d'Etudes du Bouchet (CEB), in France, to answer to real necessity of sensitivity and selectivity in detection of gases or polluted surfaces. Focusing powerful laser pulse on a surface produces the vaporization of small amount of the sample, then induces, near the focal region of the lens, high temperature plasma. By using spectral and time resolved plasma emissions, the elemental composition of the material can be determined.

The military applications of TRELIBS are the real time detection and the identification of biological and chemical agents with analysis of polluted surfaces. Another purpose of the analysis has been developed : the study of archaeological materials, like stained-glass windows and more particularly, the yellow glass. The yellow color is due to the presence of silver in paint composition. Thanks to determination of elementary composition, we can establish the original process to make the yellow coloration and the acids used before to clean the antic glass.

The main advantage of this method is that, without laborious chemical preparation, it especially provides direct analysis of solids. Only optical access to the sample is required, and sample contamination-induced risks are minimal. The LIBS technique is very promising for archaeological material. There is no problem with the sample dimension, the surface appearance, and the chemical or physical proprieties and, it's a qualitative analysis in real time of all atomic elements (contrary to X-ray fluorescence). Another advantage is that this technique can be adapted to corroded coins without cleaning them. The volume of impact is very small: diameter is inferior of 100  $\mu\text{m}$  and the depth is around 30 nm. Because this method is really rapid, it's possible to carry out many analysis in the same conditions, and thus, with a better reproducibility.

The first qualitative analysis has been achieved in comparison with X-ray fluorescence, and the results have shown that LIBS technique is really adapted to this sort of objects. Indeed, in opposition to X-ray fluorescence which is a global method, the LIBS technique is more selective and allows to analyze superficial details and to distinguish the grisaille and the glass. When analysing glass, it's necessary to create the vacuum in X-ray fluorescence chamber in order to detect light elements (Na or K) which characterize the kind of glass, and to eliminate interfering lines (if not, Ar line hides the Ag line). TRELIBS method does not face this problem: the choice of several spectral windows gives the profile of the stained-glass window composition and avoids potential problems of interfering atoms. During the analysis in X-ray fluorescence on yellow glass, made by several knowing processes, we have noted that the silver is detected only if the layer is thick : it's a real problem to antic stained glass window ! As the limit of detection is low, LIBS method detects perfectly the silver. Lastly, as all elements are detectable, it's easy to determine the light elements in order to characterize the nature of the glass. The shot repetition at the same location gives the evolution of the composition according to the depth, and it points out the heterogeneity in the material.

Our goal is now to establish a miniaturization for the in-situ analysis in military and civilian applications, to reach lower thresholds requested because of the high toxicity of CW agents and to have a minimal impact in archaeological objects with good sensitivity.

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## Quantitative Determination of the Composition of a Ceramic Sample from Shahi Zinda Necropolis (Samarkhand) by CF-LIBS

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The Calibration-Free LIBS (CF-LIBS) technique, developed and patented at IFAM-CNR, has been used for the first time for the quantitative analysis of a ceramic sample coming from the Shahi Zinda necropolis of Samarkhand (Uzbekistan). The necropolis was built at the beginning of XV century AD, after the Mongolian conquest of the Samarkhand region. The Shahi Zinda necropolis is characterised by a magnificent coverage of ceramics with different colours and distinctive decorations (see fig. 1).

One of the main problems of traditional analysis of ceramics is detaching the pigment from the substrate. Several techniques have been developed for this purpose; however, the chemical analysis is always characterised by lengthy procedures and often affected by substantial uncertainties.

With the use of CF-LIBS, we were able to sample the surface of the ceramic pigment, thus avoiding contamination from the substrate. The characteristic feature of the CF-LIBS approach, i.e. the absence of calibration curves or reference samples, allows for a fast and precise analysis of the pigments, resulting in a good agreement with the results obtained by Fabbri et al. (1999) using a specialised technique of surface acid attack and ICP analysis of the resulting solution.

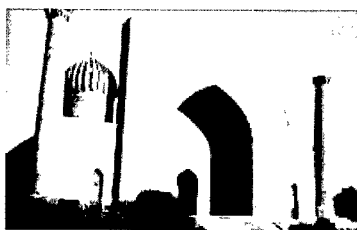


Figure 1 – The Shahi Zinda necropolis in Samarkhand    Fig. 2 – Ceramic sample analysed by CF-LIBS

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## Quantitative Compositional Analysis of Mineralised Tissue

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Mineralised tissue, i.e. bones and teeth have been found to be excellent “archives” determining living habits, nutrition and mobility of the ancient as well as the modern human. Even bones exhibiting contamination from their surrounding environment were found to maintain much of their biological signature from the living phase. This may be attributed to the fact that a number of elements incorporated in the hydroxyapatite crystals in the bone matrix leach only very slowly (see Vuorinen *et al*, 1996). Specifically, isotope ratio measurements and activity measurements for radioisotopes have been used to develop age models and link elemental abundancies to environmental factors (see e.g. Stamoulis *et al*, 1999).

Here we report on the application of Laser Induced Breakdown Spectroscopy (LIBS) to the analysis of important minerals and potentially toxic elements within bones. This theme we exemplify in detail for strontium (Sr) in biomedical and reference matrices. The choice of this element is motivated by its importance in medical, biological and environmental exposure.

It is clear that the sensitivity of LIBS may be insufficient in some cases to detect ultra-trace amounts of elements, and isotope distinction is largely impossible. However, LIBS has the definite advantage over most other techniques used for elemental analysis of bones that the spatial information is maintained, providing sort of a time evolution scale (this is completely lost in e.g. sample preparation by ashing).

In order to obtain quantitative calibration data we generated reference samples in the form of pellets with bone-equivalent material (majority compound  $\text{CaCO}_3$ ) have been pressed for generating standard calibration curves. Specifically, we added Al, Sr and Pb in the range 50-5,000ppm, relative to the Ca content of the matrix. As a possible alternative to “artificial” reference samples we attempted elemental spiking, by soaking bone fragments in a water solution containing well defined concentrations of  $\text{SrCl}_2$ . However, the LIBS measurements of said samples reveal that rather little Sr is migrating into the bone matrix confirming in reverse the slow leaching of certain elements from the bone (Vuorinen *et al*, 1996).

We have generated cross sectional maps for the absolute concentration of Sr in selected bone samples, both archaeological and modern man specimen. We would like to note, that these LIBS measurements are tied in with RIMS experiments on the same samples which exhibit improved detection limits and allow for isotope ratio measurements (Philipsen *et al*, 2000). The latter we plan to exploit to trace the radioisotopes  $^{90}\text{Sr}$  (environmental origin from e.g. the Chernobyl disaster) and  $^{89}\text{Sr}$  (used in radiological treatment of bone marrow cancer).

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## Effect of Laser Induced Plasma Etching of Enamel and Ceramic Restorations on Microleakage and Bond Strength

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The use of laser as an alternative for acid etching in surface treatment of enamel prior to sealant application is of a great importance to improve the bond strength and reduce microleakage (C. Dana et al 1996 ). UV-third harmonic of Q- switched 30 –50 mj per pulse Nd YAG laser ( $\lambda = 355 \text{ nm}$  ,  $\delta = 7 \text{ ns}$  and 30 Hz repetition rate) is used in etching of the surface of forty freshly extracted human teeth and a corresponding number of two types of ceramic restorative materials ( conventional ceramic and low fusing ceramic ), twenty of each type. The samples are divided into two groups exposed to two different energy densities, namely  $0.66 \text{ j/cm}^2$  and  $1 \text{ j/cm}^2$ . The laser beam is focused onto the surface of the rotating sample via a fused silica cylindrical lens. Two types of bonding agents, scotch bond and protec-cem, are applied for bonding the laser etched ceramic samples on the laser-etched enamel of the prepared teeth. The samples are subjected to microleakage investigation via SEM micrographs and to mechanical bond strength tests to evaluate the effect of bonding of ceramic restorations to enamel after laser etching. Results are compared to the obtained data in case of using HF instead of laser in the etching process.

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## **Improvement of Both Dental Ceramo-metal and Ceramometal Alloys-Cement Shear Bond Strength Via Laser Induced Aluminum Plasma coating**

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Laser applications in dentistry has been investigated since the 1960s (R.H. Stern et al 1964 ). Some of the literature shows promising potential for certain hard tissue applications of laser energy such as Laser coating which provides a possibility of an improved technique for the deposition of high quality metallic layers. This may be exploited in depositing a wide range of materials with minimal distortion and damage of the underlying substrate (N.B. Dahotre, et al 1995).

In the present work, thin layer of high purity Aluminum has been ablated via Nd YAG- laser pulses (  $\lambda = 355$  nm,  $\delta = 7$  ns at a repetition rate of 30 Hz ) onto the surface of three different types of precious-, semiprecious- and metal base - dental alloys . The effect of the laser ablated aluminum layer on the ceramo-metal bond is studied via SEM micrographs, EDEX micro analysis and shear bond strength measurement. The experimental results showed an improvement on the qualitative and quantitative adhesion compared to the control groups in which no laser ablation is performed. The effect of the laser plasma coating of Aluminum on cement –metal bond of the three tested alloys is also investigated for two cement types, namely glass ionomer and adhesive resin cements.

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## **Simultaneous Measurement of Laser Induced Plasma by Optical and Opto-acoustical Methods**

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A high power, pulsed laser beam, on focussing produces very high irradiance at the target sample, leading to breakdown and plasma generation (Casini et al 1991). We have made plasma diagnostics in three methods: viz,

the intensity of characteristic spectral lines from the target sample,

the integrated intensity of plasma,

the accompanying shock waves.

The targets used were hardened gall stones from the patients and a few alloy samples.

First, second or third harmonics of Q-switched Nd Yag laser of 7 ns pulse width and pulse energy (50 - 200 mJ) was focussed on to the sample, employing lens of focal lengths 50 to 500 mm. The intense plasma generated was analysed through an OMA for the spectral content and the relative intensity of lines for different operating condition. Simultaneously, the intensity of plasma was monitored by a PMT and a ceramic photo acoustic detector. The correlation between these three technique gives insights into the plasma diagnostics.

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## **The Quick and Easy Quantitative Method to Analyse Au-Ag-Cu and Pb-Sb-Sn Alloys using Homologous Concentrations and Laser Ablation-Spark Spectroscopy Technique with the Extra-Large Linear Charge Coupled Detector**

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The use of the homologous concentrations, e.g. the relative concentrations of the analysed element and the internal standard giving the equal intensity for the chosen pairs of emission lines, were previously reported for the photographic method of detection (Korneev and others, 1990). Some improvements were made subsequently resulting in very quick and easy analytical method.

The main idea of the method is to establish the homologous concentrations from the several analytical curves in given stable conditions and then use the analytical formula  $C = (\lg(I/I_2) \cdot C_1 - \lg(I/I_1) \cdot C_2) / (\lg(I/I_2) - \lg(I/I_1))$ , where  $C$  is the relative w/w concentration of the analysed element,  $I$  - intensity of its emission line,  $I_1$  - intensity of the 1st internal standard line,  $I_2$  - intensity of the 2nd internal standard line ( $I_2 < I < I_1$ ),  $C_1$  - is the homologous concentration for the 1st pair,  $C_2$  - for the 2nd.

If the concentration of the internal standard is near 100% it is possible to measure the concentration of the analysed element directly, in other cases the calculation of the dilution factor is required.

As this method no needs the weighting of the sample it seems to be the best choice for the laser ablation technique.

The practice of the method revealed that the use of the appropriate pairs of lines requires its simultaneous detection in the large spectral range. In this connection the extra-large (253,2 mm) linear charge coupled detector, formed with 9 standard elements without "dead zones" and connected to PC, as well as simple and friendly interface and software was developed.

Copper was used as the internal standard for Au-Ag-Cu, and tin - for Pb-Sb-Sn alloys.

The RSD of the method is no more than 5-10% that permits to determine the make of the alloy, analysing simultaneously with single discharge of the laser the three elements in the range from 0.1% up to 99%.

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## Determination of Precious Alloys Caratage by Laser Induced Plasma Spectroscopy

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The problem of determining the composition of precious alloys is particularly important for jewel manufacturers and their suppliers of the raw materials. In fact, the manufacturing process, in compliance with domestic and international regulations, requires a careful quality control and certification of the products that, up to now, can only be achieved by application of the traditional cupellation ("fire assay") method. This kind of analysis, although very accurate (around 0.01% in gold concentration determination) is essentially destructive and requires a number of critical measuring stages – including weighing of the sample up to fifth decimal digit, acid attack of the sample and successive weighing of the gold residual – and can be performed, therefore, only by highly skilled operators.

In recent years the need for fast determination of precious alloys composition stimulated the proposals of different alternative techniques for caratage determination, among which the following are worth mentioning: Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AE), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Neutron Activation Analysis (NAA) and X-Ray Fluorescence Spectrometry (XRF) techniques.

The purpose of this paper is to present a new and efficient technique for precious alloys caratage based on the Calibration-Free Laser Induced Plasma Spectroscopy (CF-LIPS) method. The LIPS analysis can be carried out in few minutes and in an essentially non-destructive way on samples of arbitrary shape. Experimental results showing the feasibility of the method for fast and precise analysis of gold jewelry without the need of calibration are presented. Using a new technique of LIPS spectra analysis, recently developed and patented by the Applied Laser Spectroscopy Laboratory at IFAM, we were able to obtain quantitative information about all the alloy components, including trace elements at concentration down to the order of 1 ppm. Matrix effects do not affect the accuracy of the technique.

## Characterization of Residual Dirt on Steel Plates Using LIPS Techniques

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Cold-rolled steel plate emerges from the manufacturing process with a thin layer of residual dirt that has to be monitored for control quality and effectiveness of downstream operations such as painting, galvanizing, etc. Standard characterization of this residual dirt is performed by different non-real time laboratory techniques. Recently it was demonstrated the effectiveness of an on-line photoacoustic method (G. Bilmes et al, 2000), based on optical ablation, for the recording of the total amount of dirt.

In this work, we explore the possibilities of using a LIPS-based method for a on-line measurement setup in order to develop a fast and inexpensive device for qualitative and quantitative determination of the main dirt component.

A pulsed Nd YAG – Q switched laser beam (7ns FWHM, 650 mJ) emitting at 1.06 microns impinges on the inspected steel plate producing the sudden ablation of dirt and the generation of a plasma plume. The plate was moved at constant speed across the laser beam, to ensure that no consecutive laser pulses impinge on the same spot. The integrated spectrum from the light plume was obtained using an echelle spectrograph that allowed to record it from 200 to 1000 nm. As expected, typical recorded signal consist of a discrete spectrum superimposed on a continuous background, centered at 600 nm.

In order to recognize the spectrum belonging to the dirt layer only, a sample of the dirt film was removed by applying a transparent adhesive tape on the steel plate surface and analyzing the plasma produced when the laser pulse impinges on the tape. The obtained spectrum was taken as reference for the study of the plate surface plasma, together with a data base consisting of spectral lines belonging to the most common elements that may be present in the dirt.(NSRDS-NBS, 1980).

Increasing the number of constant fluence laser shots impinging on the same plate surface spot, ablation dependent spectra are obtained thus allowing to distinguish between the dirt layer (or other manufactured deposited films) and the substrate.

According with our results, this LIPS method has promising applications for on line analysis of residual dirt on cold-rolled steel plates, and may be extended to other industrial manufacturing processes.

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## Standard-less LIBS Measurements on Aluminum Alloys

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We have applied the new Standard-less LIBS method, developed and patented by the IFAM Applied Spectroscopy group, to the analysis of aluminum alloys. The elemental composition of primary and secondary alloys usually utilized in the fusion process is particularly important for the quality of the material. The possibility of in situ applicability, the rapidity and non-destructivity of LIBS analysis make this technique ideal for on line monitoring measurements.

The experimental apparatus operating in IFAM laboratory is constituted of: a Quanta System Q-switched Nd-YAG laser (Handy 100E), delivering about 600 mJ at 1064 nm and about 100 mJ at 355 nm, in 7 ns pulses at a maximum repetition rate of 10 Hz, an optical system for focusing laser beam and collecting the emitted light, a Mechelle 7500 spectrometer by Multichannel Instruments coupled with a PCO ICCD camera. The spectrometer acquisition is delayed with respect to the laser pulse in order to reduce the contribution of the continuum *Bremsstrahlung* radiation to the LIBS signal.

The resulting spectrum is analyzed with the Standard-less CF-LIBS method.

The samples analyzed of aluminum alloy, originating from the Teksid foundry in Carmagnola (Torino, Italy), have showed some compositional differences and non-homogeneities.

## **Liquid Steel Analysis by Laser-Induced Breakdown Spectroscopy: Dynamic Effects**

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LIBS is a fast, non-contact method allowing large working distances between the sample under investigation and the detection system. These properties make LIBS applicable to process control in metallurgy. We describe an apparatus designed for rapid in-situ analysis of molten metals at variable distances of up to 1.5 m. Addition of admixtures to liquid steel results in rapid response of the system. Results about dynamical monitoring of several steel composites are presented.

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## Optimisation of On Site Analysis of Melts by Laser Spectroscopy

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Due to the important economical advantages of direct analysis of molten metals without sampling, utilisation of these methods is based on the technical and spectrochemical conditions. Accuracy, repeatability have to meet the requirements of the metallurgical process-control being not superseded by the traditional spectrometric analytical methods.

Our laboratory experiments summarised not only the possibility of analysis of liquid metals and alloys by means of the Time-Resolved Laser-Induced Breakdown Spectroscopy (TRELIBS), but the necessity of an appropriate optimisation procedure was also indicated. The optimisation procedure for the application of TRELIBS will be presented. According to the results achieved, the method can be successfully applied for the analysis of aluminium and zinc- alloy melts.

This procedure must include the choice of

- the appropriate gas atmosphere,
- the delay-time and gate-width,
- the optimum measuring method (peak, area),
- the possible correction methods (coincidences, overlapping of lines).

As a matter of fact, the molten phase need separate calibration. This fact is well demonstrated, its cause is- among other things - the change of diffusion coefficients with the temperature. Precision data can be obtained only in a narrow temperature range of the melts.

In the lecture, the results of this optimisation will be presented. For the evaluations special owner software (DATAPRO 4.2) has been used.

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## Remote Ablation and Atomic Emission Spectrometry of Stainless Steel at High Temperature

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Steel making process requires a precise supervision of the chemical composition in the molten steel bath. From the melting to the final casting steps, including the refining practices, the steel withstands several compositional changes requiring determination of the composition. The information from the laboratory is used in the workshop as a basis of an ongoing process where the time factor means productivity and consequently a decrease of the operational costs. Currently, in spite of the high level of automation in the labs, the traditional routine has been modified very little. Procedural steps such as hot steel sampling, sample cooling, sending the sample from the steel shop to the lab, cutting and surface preparation of the sample still entail an significant delay until the analytical results are available to correct the composition and continue the process.

On the other hand during hot rolling stage, steel in form of slabs or billets could be processed incorrectly due to errors in their identifications what would mean an inadequate rolling temperature and then a severe breakdown on the materials. A total control of the steel grade prior to the hot rolling step would ensure the suitable metallurgical treatment of the material and avoid any chance of mixing up.

An instrumental approach intended to minimize or eliminate such risky and lengthy hot-sampling operations is presented based on laser-induced breakdown spectrometry (LIBS). A prospective study has been carried out by using a Q-switched Nd:YAG laser operating at 1064 nm to create a plasma on an AISI 304L stainless steel sample placed inside a laboratory oven. The steel sample was 51.5 cm away from the focusing lens. The temperature of the samples ranged from 25°C to 1200 °C. The plasma light was collected by to a fiber optic bundle and spectrally analyzed using a spectrograph equipped with a CCD camera.

The effects of sample temperature in the formation of laser-induced plasma have been studied in terms of its spectral features as well as the morphology of the ablated craters. A significant dependence of signal emission intensity with the sample temperature has been found. Depth profiling of stainless steel samples for several temperature conditions was performed. Results have revealed changes in the superficial composition at temperatures above 600 °C due to the formation of a slag layer of variable thickness mainly composed by chromium, iron and manganese oxides.

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## Depth-resolved Profiling of Galvannealed Steel Samples by Laser-Induced Breakdown Spectroscopy

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Laser-Induced Breakdown Spectroscopy (LIBS) is a suitable and powerful method for direct in-process measurement of elements concentration and depth-resolved profiling in material analysis and metallurgical applications.

A low cost laser induced breakdown spectroscopy system was developed. This system is composed by a Nd-YAG laser (irradiance:  $\sim 10^9 \text{ W/cm}^2$ ), an optical focusing system, a polychromator and an optoelectronic processing device. A linear CCD camera, data acquisition electronics and associated control software were specifically developed to capture and process the plasma's spectral lines intensity. The technical characteristics and mechanical design of the system were oriented to "in situ" surface analysis of solid samples. Using an optically transversal remote sensing experimental setup, it is possible to select an optimized place, through plasma's plume, to increase the spectral signal to noise relationship. This transversal spatial resolution substitutes the necessity to use a time-resolved spectroscopy system.

The intensity of plasma's spectral lines depends not only on the specific element concentration but on the power density and local plasma temperature too. To minimize the influence of the plasma's spectra line intensity changes with beam penetration and to improve the depth resolution, a normalized algorithm was proposed and tested. The advantages of this approach in LIBS technique, to resolve qualitative and quantitative analysis of multilayered samples depth profiles, were demonstrated.

Different types of galvannealed steel samples were quantitatively studied by monitoring the specific Zn and Fe emission intensities with depth profiles. Using a differential scan calorimeter (DSC), the galvannealed steel samples were thermally modified. Their interfaces distributions changes were studied and correlated by LIBS deep-profile analysis, by energy dispersion spectroscopy (EDS) and scanning electron microscopy (SEM). These techniques allowed the estimation of the ablated mass per shot and the penetration rate. Possibilities of employing the developed LIBS system to control metallurgical processes are also discussed.

## Analysis of detectors for medical imaging with Laser Induced Plasma Spectroscopy

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### Abstract

We are studying the spectroscopic and imaging properties of various thickness GaAs pixel detectors for medical imaging applications in different energy ranges. A 200 $\mu$ m thick GaAs pixel matrix bump-bonded to a dedicated VLSI photon counting chip (PCC) has already been tested for digital mammography applications using a clinical tube (mean energy 20 keV). For more energetic photons, as in nuclear medicine field, a thicker detector is required in order to obtain a satisfactory detection efficiency. We have then chosen a 600 $\mu$ m thick detector and tested a prototype based on this detector and the PCC using radioactive sources ( $^{241}\text{Am}$ , 60 keV photons and  $^{99\text{m}}\text{Tc}$ , 140 keV photons). We have evaluated the imaging properties (as Modulation Transfer Function and Point Spread Function) of our systems and realized images of a mammographic and a thyroid phantom, respectively. We have made also a comparison with standard systems (film-screen for mammography and gamma camera for nuclear medicine). The results obtained are very good, but we encountered some problems related to the aging of detectors and contacts and to the handling of the detector in particular during the process of bump-bonding to the electronic chip. So we have used the Laser Induced Plasma Spectroscopy technique in order to indagate about these phenomena. In this work we present the results obtained about the front and back surfaces of a GaAs crystal free of contacts and about the Ohmic and Schottky contact.



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## **LIBS Capabilities for Semiconductor Characterization: A Critical Comparison with Well-Established Analytical Techniques**

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Semiconductor research, both applied and fundamental, deals with high purity artificially synthesized materials, and needs therefore high analytical sensitivity characterization techniques. III-V or II-VI ternary and quaternary alloys are commonly employed in growing structures for micro- and opto-electronic devices, and a very precise control and determination of their composition is required in order to obtain the desired properties. High Resolution X-ray Diffraction (HRXRD) techniques are normally used to determine the semiconductor compositions, often associated with Rutherford backscattering spectrometry (RBS). Another important issue is to determine the dopant (intentionally added) or contaminant (unintentionally added) impurity concentration, with high detection sensitivity required, often in the ppm and sub-ppm range. Secondary Ion Mass Spectrometry (SIMS) is the widely adopted characterization technique to this aim.

Laser Induced Breakdown Spectroscopy (LIBS) has the potentiality to face these and other typical semiconductor analytical problems in a flexible way, due to simultaneous multielement analysis capability, detection limits in the sub-ppm range, and calibration-free spectral analysis, though some instrumental issues have to be addressed. In this paper we critically review the existing literature on semiconductor LIBS application; furthermore we present some new experimental results on the comparison between LIBS and other well-established semiconductor characterization techniques, drawing some conclusions about the use of LIBS for this important class of material.

## **Pu-239/Pu-240 Isotope Ratios Determined using High Resolution Laser Induced Breakdown Spectroscopy (LIBS)**

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Isotope ratios for plutonium may be determined through direct observation of atomic emission spectra at high resolution. The isotope shift for Pu-240/Pu-239 of +355 milliwavenumbers for the 594.52202 nm plutonium atomic line has been resolved from a laser induced plasma using a 2-m spectrometer in double pass mode and an electronically gated, intensified CCD (ICCD) camera. The ratio of integrated peak areas match known isotopic ratios to within 0.1%. The measured linewidths of < 0.0065 nm for these plutonium atomic emissions are substantially less than reported uranium intrinsic linewidths of 0.012 nm (Pietsch et al., 1998). The plutonium emission was generated using the 1064 nm fundamental from a Nd:YAG laser at a power density of 63 GW/cm<sup>2</sup> under 100 mtorr of He, whereas the uranium emission was reportedly generated using a 308 nm XeCl excimer laser at 0.46 GW/cm<sup>2</sup> under 20 mtorr of air. Analysis of the instrumental line broadening limit suggests that the intrinsic linewidth of plutonium emission under these conditions is still less than the measured linewidth.

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## Sodium Aerosol Detection in High Temperature Sodium Leakage Field using Laser Induced Breakdown Spectroscopy

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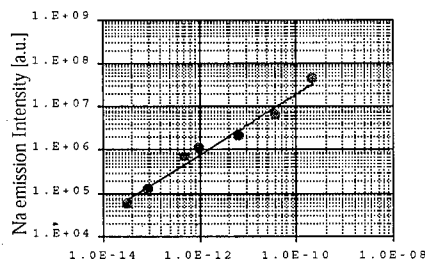
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### 1. INTRODUCTION

Sodium leakage, which might cause fire accidents in Fast Breeder Reactor Plant, should be detected as soon as possible while it is minimal. For this reason, experiments to grasp sodium leakage behavior, which might be practically take place, were conducted and sodium leak detection system using laser induced breakdown spectroscopy was improved.



Na concentration [g/cm<sup>3</sup>]  
Fig.1 Calibration curve

### 2 RESULTS

The LIBS+ICCD system was configured in order to lower cost and minimize maintenance, and performance tests were conducted. This system can measure the sodium/nitrogen atomic ratio in gas, so a system to measure absolute sodium concentration online was constructed. Figure 1 shows the calibration curve for sodium concentration. In result, the system has  $5 \times 10^{-14}$  g/cm<sup>3</sup> detection sensitivity.

By conducting proof test, behavior of sodium aerosol in practical system was examined. And for using improved detectors, the possibility of detection the actual sodium leak was confirmed.

### 3. ACKNOWLEDGEMENT

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## Application of LIBS in Civil Engineering for the Analysis of Concrete

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An important field for the application of LIBS is the investigation of the chemical composition of building materials (Wiggenhauser 1995, Pakhomov 1996). At the Federal Institute for Materials Research and Testing for several years such investigations have been performed (Wiggenhauser 1997). This contribution deals with the analysis of concrete.

Building materials like concrete, cement, mortar, bricks and natural stones are naturally inhomogeneous. Using concrete as an example the characterization by LIBS must take into account the local variation of the element composition using a statistical analysis. For the quantitative analysis of the dominant elements (Ca for cement matrix, Si for aggregates) a large dynamic range and a high spectral resolution are required. A differentiation between concretes made of different cement types is complicated by the natural variation of the element content in the base material.

With each laser pulse, a varying ratio of cement and small aggregates or - when hitting a larger aggregate - only the aggregate composition is detected.

Therefore, line and area scans and a statistical data analysis are used. The results are visualised by using a modified Rankin diagram.

This data analysis allows to characterise such inhomogeneous materials as concrete. It is e.g. possible to identify the type of cement and the type of aggregates used. Also carbonation can be investigated taking the carbon content into account.

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## **On-line Iron Ore Slurry Monitoring for Real Time Process Control of Pellet Making Processes Using LIPS**

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Chemical composition of iron ore pellets has a significant impact on their quality and commercial value. LIPS technique has been extensively tested on line, at industrial pellet making plants. It proved successful at measuring carbon, silica, calcium, magnesium, and aluminium contents of different iron ore slurries prior to filtration and pelletizing. For this specific application, the sensitivity of the technique compares with the one obtained from dedicated chemistry laboratory. But LIPS real advantage is that the results are delivered continuously and in real time compared to periodic sampling and standard analytical delays of more than one hour. Consequently, LIPS gives a more representative reading of the state of the process, particularly when rapid perturbations occur, and allows better feedback correction for process optimisation and quality improvement.

Special attention is given to the fact that the detection system, with specific setting, gives direct measurement for either graphitic carbon (coke breeze addition) or total carbon (flux addition and/or natural carbonate). Since graphitic carbon content is a key factor for the pellet quality, research has been focused on its measurement.

LIPS shows a good sensitivity at detecting small variations, but it is sometimes difficult to establish absolute calibration curve when chemical compounds associated with targeted elements change. In those cases, results are calculated using a multivariable calibration tool that corrects for matrix effects, and evaluates a confidence level based on expertise for each measurement.

Current research is aimed at the development of commercial equipment for continuous industrial use.

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## Fast Deuterium Analysis of Water Samples by LIBS

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The deuterium composition of natural waters, along with other isotopic and chemical data, is a fundamental parameter in geochemical studies. For example, 1) the deuterium concentrations in the water discharged from geothermal wells is useful to discriminate its possible source; 2) temporal variation of the deuterium content in the steam condensates from high-temperature volcanic fumaroles may indicate changes in the degassing mechanism from the related deep magma, or different contributions from shallow groundwater to the fumarolic conduits linked to changes (e.g. earthquake-induced) in the fracture permeability of the rocks.

The deuterium content in a water sample is commonly obtained by a two-steps method. The water sample reacts with zinc shots at 450°C to give hydrogen, that is subsequently transferred to the mass spectrometer for analysis.

Recent preliminary applications of the LIBS technique by the Applied Laser Spectroscopy Laboratory at IFAM to deuterium-rich water samples revealed that the deuterium and hydrogen spectral lines can be easily distinguished if the deuterium concentration is higher than about 5 %. More work will be necessary in the future to decrease this lower limit in the deuterium content.

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## Time Resolved and Gated Measurement Spectroanalytical Laser Spark in Liquid

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In this paper we describe the temporal and spectral extension of LIBS to the direct sampling of liquid media, using a 10 Hz Nd:YAG laser, and a chain of detection which is composed by a PMT, a monochromator, a Box-car Averager and a data acquisition system. In our application, we have monitored Sodium Chloride (NaCl) in water at concentration below 1mg/L, which is below 0.39 ppm for Na. We studied the time evolution of the emission spectra of a Sodium chloride in solution. We show that the strong plasma background emission at 0.6  $\mu$ s delay is strongly reduced after 1.2  $\mu$ s delay, to allow to detect the useful signal.

To detect the useful signal, we have to optimise the delay of acquisition start regarding to the plasma emission as well as the acquisition duration.

For needs of our experiments we have to perform a system that allow the temporal and spectral resolution of the studied plasma. A OMA detection system (Optical Multichanal Analyser), is the most adequate for our experiments needs.

These facilities are equipped of systems called ' Intensified Gated Charge Coupled Device (ICCD) Camera'. Researchers as : Yamamoto [1996] (CCD 256x1024 arrays detectors), Knopp [1996] (OSMA array detector 1024 linear Si photodiode), Ito [1995] (Photodetector Multichanal, SMA Princeton), Bescoses and Urena [1994] (Optical Multichanal Analyser OMA3), Vlasov [1991] (Optical Multichanal Analyser, OSA), Kitamori [1989] (1024 photodiodes arrays)

The scientific literature we have access often gives reference to experiments that are achieved with a Boxcar Averager detection system which arranges possibilities of temporal resolution but no spectral [D. Cremers [1984]]. This last, the spectral resolution, will be achieved by using a monochromator. However this way to proceed compelled us to not do any resolute measures simultaneously in time and in frequency and times of acquirement will be lengthened.

The identification of the neutral atom lines or ionised once makes himself from tables and Grotrian diagrams [A.A.Radzig, 1985] or energy- levels diagrams.

Limits of detection for Na I (0.39ppm), Li I (8.3ppm), Ca I (36ppm), Ba II (0.33g/l), and Al I (2g/l), at their characteristics lines, in aqueous solutions were established with the use of a 10 Hz repetitive spark.

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## **Characterization of Hydrocarburic Rubbers by Laser Induced Breakdown Spectroscopy**

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The polyolefins, a family of insulator polymeric materials, are widely used in industry because of their electrical and mechanical properties. Among these, the best insulators are polyethylene and the ethylene-propylene rubbers (EPR), used also for very high voltage cables. The EPR is produced by catalytic polymerization, and its electrical properties depend on the amount of residual catalyst.

A reliable traditional method to test the purity of the rubbers is based on extended boiling of the samples in water, followed by gravimetric measurement of water absorption and checking of the residual insulating capacity. The ultra pure hydrocarburic polymer absorbs a negligible quantity of water, whilst the metallic salts are very hydrophilic, jeopardizing the long lasting performance of the cables in the real environments.

Several rubber types, produced by different factories, have been checked for utilization in medium voltage electric cables insulators. In the present paper we report the comparison between the results obtained by this traditional method and the ones obtained by LIBS measurements. The LIBS technique is extremely fast and reliable, confirming the information about metallic traces and in a good agreement with the amount of absorbed water. In some cases the LIBS analysis allowed to obtain information about the catalytic system used for manufacturing the polymers.

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## Analysis of Paper by LIPS

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We describe a method based on a LIPS technique (Laser-induced Plasma Spectroscopy) for analysis of material distributions in paper. Paper consists of small cellulose fibers which are bound together by hydrogen bonds. In some grades, inorganic pigments (fillers) are added in order to improve the opacity and surface properties of paper. Paper may be coated by a porous layer of pigments and adhesive to further improve its surface properties. The purpose of coating is to fill voids in the base paper and give a smooth surface. The material distributions in paper and paper coatings are important factors which determine the properties and quality of paper. The key considerations in using LIPS-analysis here are to i) record a spectrum from every pulse, ii) use a pulse energy as low as possible, in order to map a material distribution with sufficient high spatial resolution. The spatial resolution in analysis of paper coatings is typically 100  $\mu\text{m}$  in lateral and 1  $\mu\text{m}$  in depth. For filler analysis, the resolution is  $\sim 3 \mu\text{m}$  in depth because of less dense material.

The elements that are primarily monitored are C, Ca, Si, Al, and Mg. Emissions of carbon originates from organic materials (binders or fibers) and  $\text{CaCO}_3$ . A carbon line has been monitored only in analysis of binder distribution on the paper surface. Pigments most commonly used in paper are calcium carbonate, clay, and talc. Emission line intensities of elements of these pigments represent amount of pigments at particular point in the sample. A typical measurement of light weight coated paper (LWC) is a 5 cm line with 0.1mm steps and 20 pulses/point. This results in the generation of 10,000 spectra from a single sample, a process that takes 20 minutes.

From the data we can calculate the coat weight distribution in paper. LIPS is especially useful in analysis of multilayer coatings. Coating layers can be distinguished if they differ in their composition.

The setup used is composed of ArF-excimer laser (193 nm) for generation of cold plasma from the sample, a spectrograph combined with an ICCD-detector for time resolved spectroscopic measurements (typical time delay being 50 ns), and a computer controlled sample holder for mapping. Analysis is carried out in ambient air at atmospheric pressure.

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### **3-D Distribution Analysis of Platinum, Palladium and Rhodium in Auto Catalytic Converters Using Imaging-Mode Laser Induced Breakdown Spectrometry**

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There is now overwhelming evidence that the urban environment is being contaminated by platinum, rhodium and palladium derived from catalytic converters installed in motor vehicles. It is apparent that these metals are being released into the environment adsorbed on small particles as a result of surface abrasion of the catalytic structure during car operation. Laser-induced breakdown spectrometry (LIBS) is reported here as an effective technique to describe the volume distribution of these metals in converters. Using the second harmonic output of a Nd:YAG laser and a CCD-based atomic emission spectrometer, LIBS is used in multielemental, imaging-mode to permit the simultaneous analysis of the several elements present in the converter, including the internal standard. The data are reported with a lateral resolution of 1.75 mm over a fresh catalytic structure which is 128 mm long. The concentrational variability of the platinum group metals (PGMs) varies in the range ~3-23% relative standard deviation depending on the element, the substrate and the direction investigated. The causes of the dispersion observed are discussed.

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## Spectroscopic Diagnostics on CW-laser Welding Plasmas of Aluminium Alloys

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Laser welding of aluminum alloys is a challenging application for both the automotive and the aerospace industries. Aluminum structures obtained with this technique are lighter than their counterparts made with other materials and still present excellent mechanical properties. However, the complexity of the aluminum laser-welding process induces a number of weld defects that have prevented a wider implementation of the technology at the factory level.

Although a number of works have been devoted to elucidate the phenomena having place during laser welding, to the authors' knowledge, a systematic spectroscopic study has not been carried out so far. In the present work, the plasma light emitted during high-power CO<sub>2</sub> laser welding of a 6013 aluminum alloy was collected and spatially integrated by means of a lens focused into a 200 µm fiber optic. The end of the fiber was coupled to a spectrograph equipped with gratings of 300, 1200 and 2400 grooves/mm. The dispersed light was detected with a 1024x128 CCD system cooled to -20°C. Data processing was carried out with specific software developed for the application. A transient recorder was used to record the signal from a fast laser-power monitor and the sync signals from the CCD and a fast speed video-camera capable of up to 18k fps. A high power laser diode was used to provide adequate illumination to the fast speed camera through a fiber optic.

Process diagnostics have been carried out based on the spectrometric results. The results of temperature measurements are discussed and certain fluctuations in aluminum plasma emissions have been correlated to the occurrence of weld defects.

## Nanoparticles, an Interesting By-product of Laser Induced Argon-Spark

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When LIBS is performed under certain conditions, the sample material is not “ablated” but rather “sputtered”. Under these conditions not only does one obtain a very reproducible optical emission signal for LIBS measurements, but also as by-product an aerosol with extremely fine particles, representing accurately the sample!

These particles are the result of recondensed vapors which build clusters with a dimension of 5-8 nm. The conditions for this Laser-sputtering will be discussed: wavelength of Laser, choice of gas and pressure, pulse energy and specific power.

The device for producing these particles has been named LINA-Spark™ Atomizer and is protected by international patents.

The main application of the LINA-Spark Atomizer is direct bulk-analysis of solid samples by ICP-OES and ICP-MS: it permits to produce a dry aerosol from any solid sample, avoiding thus the often tedious and labor-intensive dissolution of the sample. The dry aerosol is introduced into the ICP, where the particles are well vaporized and ionized due to their extremely small dimension.

Examples of bulk analysis with the LINA-Spark Atomizer and ICP will be presented.

As the Atomizer removes the material from the surface, layer by layer, one can also perform “surface” analysis, by measuring the removed elements on-line in the ICP. Contamination on Si-wafers has been measured with a detection limit  $< 10^9$  atoms / cm<sup>2</sup> with an ICP-MS.

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## Detection of BN Radicals by Emission Spectroscopy in a Laser-Induced Plasma.

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Material ablation produced by a pulsed-nanosecond laser beam with an incident energy density of about  $10 \text{ Jcm}^{-2}$  on the target surface gives rise to plasma formation with relative high initial ionisation stage. Typical values of electron density and temperature in the plasma plume, measured at a delay of 100 ns after the ablating laser pulse, range from  $10^{17}$  to  $10^{18} \text{ cm}^{-3}$  and from 1 to 2 eV, respectively. With respect to ablation of non-metal targets like graphite and boron-nitride, the density and temperature values obtained for metal targets are higher because of the low ionisation potential of metal atoms favouring plasma ionisation. In vacuum or low-pressure atmospheres, the ablated vapour plume cools rapidly down, as a result of adiabatic expansion, reaching a temperature of about 0.5 eV at 1  $\mu\text{s}$  after the laser pulse. According to this temperature evolution, the plasma plume is essentially formed by ionic species and neutral atoms during its early stage, while molecular species are formed afterwards mostly by three-body recombination. Mass spectrometry [1] and optical emission spectroscopic measurements [2] have shown that the densities of diatomic species formed by chemical reactions depend strongly on the dissociation potential of the diatomic molecules. Thus, nitride molecular formation is hardly achieved as the dissociation potential of these species is much lower than that of molecular nitrogen. On the contrary, oxide molecules are efficiently formed as their dissociation potentials are higher than that of molecular oxygen. In this context, time- and space- resolved emission spectroscopy have been performed to study the plasma induced by pulsed-laser ablation of a boron-nitride target in low-pressure nitrogen or argon atmospheres. The response of the spectroscopic apparatus as a function of wavelength has been calibrated by a tungsten lamp in order to quantify the densities of excited species in the plasma. Beside the emission from ionic and atomic boron and nitride species, very low emission of vibrational BN radical bands has been observed. From these spectra, the plasma temperature and the species densities have been estimated. The results contribute to a better understanding of gas-phase reactions in laser-induced plasmas and of reactive pulsed laser deposition (RPLD).

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## Molecular Spectra Analyses in Laser-Induced Plasmas for Rotational- and Vibrational- Temperature Determination

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A plasma in local thermal equilibrium is characterised by one unique temperature which determines the distributions of kinetic and internal energy of all plasma species. Out of local thermal equilibrium, the population densities of electronic states do not follow the Maxwell-Boltzmann law and the velocity distributions of the plasma species are generally mass dependent. In some cases, the collisional rates are sufficiently high to establish a collisional equilibrium between species of the same mass, but too low to establish an equilibrium between particles of different mass. In this case, the plasma is characterised by several temperature values corresponding to species with different mass. In particular, the electron temperature may differ from temperature of heavy particles as a consequence of the low electron mass. Plasmas induced by pulsed nanosecond laser ablation are characterised by a strong collisional regime during the first tens of nanoseconds (Knudsen layer) while the collisional rates strongly decrease during the quasi adiabatic plume expansion. Thus, this plasma undergoes the evolution from an initial state in a near local equilibrium through to a plasma out of equilibrium. In this context, measurements of vibrational- and rotational- temperatures of molecular species within the laser-induced plasma are useful for the understanding of the collisional processes occurring in the plume.

The present study deals with time- and space- resolved optical emission spectroscopy during pulsed laser ablation of different targets (Al, BN, C, Ti) in either nitrogen, ammonia or oxygen low-pressure atmospheres. Particular attention has been paid to the formation of molecular species resulting from chemical reactions between the ablated material and the ambient gas. The emission spectra of AlO, BN, C<sub>2</sub>, CH, CN, NH and TiO have been observed and analysed by computer simulations of the rotational-vibrational structure of each molecular spectrum. As a result, a complete picture of the time- and space- evolution of the rotational and vibrational temperatures has been obtained. The results are useful for a deeper insight in the chemical processes occurring in the laser-induced plasma and their role during thin film deposition by reactive pulsed-laser ablation.

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## Synthesis of Powders and Films using Laser Spark Atomization

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The evaporation of material under conditions analogous to LIBS results in the formation of nanosized particles in the 5-10 nm range. Uniform films made out of interconnected particles can be recovered on a substrate. The essential features of the films are as follows:

- relatively high deposition rates in the order of  $\mu\text{mmin}^{-1}$  are achieved using argon as carrier gas at atmospheric pressure at flow rates of about  $1\text{ lmin}^{-1}$ .
- the primary particles consist of nanoparticles in the 5-10 nm range showing partial crystalline ordering
- the films have a tri-dimensional web-like structure and show a porosity of about 95%
- the porosity and pore sizes can be modified by the carrier gas flow rate

We have applied Laser Spark Atomization, LSA, to the formation of particles and films using various target materials, including refractory ceramic materials (alumina and zirconia), luminescent and transparent conducting materials (zinc sulfide and tin dioxide), and cathode materials used in lithium ion battery technology (lithium manganese oxide). The details of the microstructure of these films were examined using scanning electron microscopy, SEM, and high resolution transmission electron microscopy, HRTEM. All LSA-deposited films showed a similar web-like, tridimensional structure formed by the interconnecting primary particles. The latter exhibited nanocrystalline domains which growth could be monitored in further annealing experiments. These results can be of great interest for analytical LIBS as well to the coupling of LSA with elemental analytical techniques (ICP, ICP/MS). The measurements of the film thickness used micro-X-ray fluorescence spectroscopy.

The deposition of thin films from other materials, i.e. silicon, carbon and some polymers was also achieved recently.

Silicon nanoparticles were shown to consist of pure Si nanocrystallites, without any detectable silicon oxide formation. By varying the atmosphere during atomization, "reaction bonding" could be achieved, i.e. reactions of the atmosphere gas reacts directly with the atomized particles. We could thus form controlled amounts of silicon oxide by varying the oxygen content in the carrier gas, whereas silicon nitride formation readily occurred when nitrogen was substituted for argon as a carrier gas.

Carbon films were deposited using a pyrolytic graphite target displaying a novel phase of carbon consisting of curled carbon nanotubes, so-called nanocurls.

Recent progress in the deposition of porous polymeric films will also be reported.

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## ***In-Situ* Monitoring Of Pulsed Laser Indium-Tin-Oxide Film Deposition By Optical Emission Spectroscopy**

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We performed optical emission spectroscopy to monitor the plasma produced during the ablation of indium-tin-oxide target in different oxygen pressure conditions using pulsed nanosecond UV laser. Molecular bands of InO was identified in the fluorescent spectra produced by pulsed laser ablation. InO line monitoring allowed to obtain the optimal conditions for good-quality ITO film deposition. We demonstrated that it is possible to correlate InO line spectroscopic parameters with the conditions required to fabricate a high-conductivity and high-transparent ITO thin film. In particular, low resistivity ( $10^{-4}$ - $10^{-3} \cdot \text{cm}$ ) was obtained in films deposited at room temperature by regulating oxygen pressure into the chamber in order to keep the InO line amplitude to a predetermined value.

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## Plasma Assisted Pulsed Laser Deposition for the Production of Films for Optical Application

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The flexibility of the experimental set-up and the large quantity of condensed matter material that can be treated by laser, make PLD (Pulsed Laser Deposition) a very promising technique for thin films production. Anyway at the moment only few industrial applications concerning the semiconductor technology are available. Indeed the fundamental limitation to the PLD technique is that, during the ablation and the production of the plume, macroscopic particulates are ejected too, affecting the quality and the property of film obtained by the plume re-condensation. This disadvantage is particularly evident for high refractive index target material because of the penetration of laser radiation to the target bulk causing the sublimation of internal layers and so the macroscopic ejection of superficial material.

In this work it will be shown that plasma assisted PLD (PAPLD) allows to avoid this disadvantage and to improve the quality of the deposited film for what concerns the stoichiometry, the morphology and the deposition rate. The target materials investigated are titanium dioxide and chalcogenide glass doped with praseodymium for optical application. The experimental set-up used is typical PLD system where the substrate holder and the target holder are respectively the RF and the grounded electrode. Transmittance and m-lines prism coupling was used to characterise the optical property and Scanning Electron Microscopy analysis to study the morphology. The chemical composition was defined by X-ray Photoelectron Spectrometry and by Energy Dispersive System.

## LIPS and LA-ICP/MS Simultaneously: Which Information do we get?

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Despite the enormous potential of LIPS demonstrated in the last decade it is still not a widely used standard analytical technique for solid sampling. In the field of solid elemental analysis, particularly in spatially resolved analysis, Laser-Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) can be considered as the approved standard technique for trace element analysis in solids. Since LA-ICP-MS and LIPS are based on the same laser-sample interaction, the combination of both techniques is an approach to combine the information of two different analytical results. The advantage of this combination can be a fundamental insights into the ablation process, the mass transfer in ICP-MS, the calibration and verification of analytical results and possibly some more detailed understanding of elemental fractionation, which is still one of the most limiting processes in LA-ICP-MS [1].

In addition to a 193 nm Laser ablation system combined to an ICP-MS [2] an echelle-spectrograph coupled on an ICCD-camera was installed for direct observation of the laser plasma in the ablation cell (the details of this spectrometer are subject of an other contribution) [3]. This plasma was created by an excimer laser ( $\lambda = 193$  nm) equipped with a beam homogenizer, allowing a highly uniform, head top profile with defined crater diameters between 4  $\mu\text{m}$  and 120  $\mu\text{m}$ . For optimum ICP performance also the gas stream in this cell (Ar or He) was controlled precisely. These controlled ablation conditions lead to extremely low standard deviations of the LIPS signals, which indicates a major influence of the beam delivery onto the sample surface. On both systems multielement analysis from the same sample were acquired. Various geological samples (minerals), polymer and glass samples were analysed using simultaneously detection (echelle spectrograph) and fast sequential detection (ICP-MS). It will be shown that the limits of detection achievable in ICP-MS are superior for trace and ultra trace elements. However, the controlled ablation process allows leads to improved stability of the signal intensities recorded by LIPS.

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## Multi-technique system for Pigment Analysis in Cultural Heritage

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The wide availability of optical sources and small, cheap spectral detectors has produced, in the last decades, a great development of analytical spectroscopic techniques, that have been successfully applied in the field of Cultural Heritage conservation and study. Among these, we can indicate Laser Induced Fluorescence (LIF), micro-Raman spectroscopy, reflectance spectroscopy in the near infrared (NIR) and Laser Induced Breakdown Spectroscopy (LIBS). These techniques have been consolidated by years of laboratory applications and in field operation. The major advantages of spectroscopical techniques are their intrinsic speed and the possibility of obtaining information on the material used in Cultural Heritage in situ, non-invasively and in real time. The intrinsic complexity of the materials used in Cultural Heritage, the variety of pigments/binders used and their degradation, do not allow indicating a single technique to be used in all the situations. This is due to the nature of the different techniques (for example, micro-Raman, LIF and NIR give non quantitative information on the molecular composition of the material, while the LIBS technique is quantitative, although elemental). It's thus interesting the development of a prototype capable of operating in situ, giving in real time information on both the molecular and elemental composition of the artwork under study.

The four techniques proposed in the integrated instrument are complementary both for the information that they give (molecular composition of pigments and binders in case of micro-Raman, LIF and NIR, elemental composition for LIBS) and for the different fields of applications. Raman microscopy is very selective; however, the Raman signal is in general very low, and tends to be masked by fluorescence (organic pigments and binders are particularly difficult to individuate by Raman). On the other hand, LIF and NIR spectroscopy, less selective and specific than Raman, are more sensitive just in the above-mentioned class of pigments and binders. Finally, the LIBS technique does not give direct information on the molecular composition of the pigments, but allows for a precise quantitative determination of the elemental composition of the material under analysis, with a dynamic range from major components (%) down to traces (ppm).

The instrument proposed has no equivalent either in laboratory use or as a commercial instrumentation. In the past LIBS/micro-Raman and LIBS/LIF measurements have been performed, on the same sample, but in any case using different instruments [1-3]. A proposal has also been presented for LIBS/LIF analysis for environmental diagnostics (polluted soils and water)[4].

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## Development of a LIBS Prototype Instrument for Future Missions to Mars

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Presently, a series of space exploration missions are being planned for launch in the early part of the 21st century which will include landings on asteroids, comets, the Moon, and Mars. The goals of these missions are to return extensive physical and chemical data regarding these bodies. Currently, for elemental analyses, either x-ray fluorescence or the APXS system, the latter deployed recently on the Sojourner Mars rover, are the methods of choice. These instruments, however, provide only in situ analysis, that is, the instrument must be in close proximity (i.e. 1 cm) to the targeted sample. For instruments on board a landing craft, analyses are therefore limited to the immediate vicinity of the landing site. More far ranging measurements can be carried out with the instruments on board a rover, but the rover must still be moved to the selected analysis site, a time-consuming process. A method of elemental analysis that permits measurements at stand-off distances, however, can greatly increase the scientific return of these missions. Here stand-off is taken to be a distance up to tens of meters. Laser-induced breakdown spectroscopy (LIBS) is a method having this capability. The LIBS plasma, formed by focused laser light, can be directed to a remotely located sample to perform a measurement at a distance from the lander or rover. This capability, coupled with the rapid analysis times offered by LIBS, will increase sample throughput significantly. At Los Alamos National Laboratory, LIBS is currently being developed for NASA's Mars Instrument Development Program. Characteristics of LIBS for use under Mars atmospheric conditions will be presented along with analytical figures-of-merit for the detection of major and minor elements of geological interest. In addition, the results of a recent field-test in the Nevada desert of a preliminary prototype LIBS instrument on board a rover will be described.

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## **Stark-Broadening Coefficients of Copper Lines Measured in a Plasma Produced by Pulsed-Laser Ablation**

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Plasma analysis during pulsed UV-laser ablation of a copper target in either hydrogen or argon low-pressure atmospheres have been performed using time- and space- resolved emission spectroscopy. The radial distribution of spectral line emission from metal vapour and ambient gas species have been investigated by means of Abel inversion. The electron density of the plasma was deduced from the Stark-broadening effect of ambient gas lines while the electron temperature was deduced from the intensity ratio of copper lines. As a result, the Stark-broadening coefficients of several spectral lines of neutral and ionised copper have been determined. Furthermore, the spectroscopic measurements give information about the vapour-gas interaction which is useful for the understanding of pulsed-laser ablation and its applications like thin film deposition, surface analyses, etc..

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## **A Closed-loop Controller for Laser Coatings Removal Systems**

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The purpose of this recently completed US DOE-sponsored program was to develop, test and integrate a complete feedback control system with the F2 Associates laser-based paint removal system. The control system is composed of fiber optics mounted directly in the laser scanner head viewing the laser-induced plasma, a field-hardened lead monitor, a control algorithm, and a DC voltage output to the scanner head motion control mechanism. The goal of the feedback control system is the optimization of the coatings removal process, thus enhancing the economics and minimizing substrate damage.

The coating removal monitor was designed for lead-based paint, but is also readily used to monitor removal of epoxy coatings and other surface organic matrices. Since the degree of surface cleanliness is identified by direct measurement of residual contamination concentration, the monitor can be used for challenging cleaning operations such as selective topcoat removal, the efficient removal of highly toxic species from substrate pores, and simple upgrade for the measurement of other metallic species.

In this presentation, we will present test results of lead paint removal optimized to achieve HUD standards and we will discuss the economics and commercial opportunities for laser-based coatings removal.

## Emission Spectroscopy Studies of Carbon Plasma in Nitrogen Environment in Carbon Nitride Synthesis

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The study of carbon plasma in nitrogen environment has been made by emission spectroscopy in order to optimise the deposition parameters for carbon nitride thin films.

In the present work, we study the spatio-temporal evolution of  $C^+$  specie at 426.7nm, neutral carbon specie at 247.8nm, the (0,0) Swan system band head at 516.5nm, the (0,0) band head of the CN violet system at 388.3nm, the (0,0) band head of the first negative system of  $N_2^+$  at 391.4nm, the ionised and neutral atomic nitrogen at 399.5nm and 735.4nm respectively, at 1 mbar of nitrogen and at  $8J.cm^{-2}$  and  $35J.cm^{-2}$  laser fluences.

The plasma is created by a Q-switched Nd-YaG laser beam of 1.06 $\mu m$  wavelength and 25 ns pulse duration. The laser is focused on a rotating pure graphite target at an incidence angle of  $45^\circ$  through 30cm focal lens. The target chamber is evacuated at  $10^{-6}$  mbar and then is filled with 1 mbar nitrogen. The luminance plume of plasma is optically imaged at  $90^\circ$  along the normal on the 100 $\mu m$  entrance slit of Spex spectrometer with a magnification of 1 giving a spectral resolution of 0.08nm.

By comparing the transient maximum emission intensity of  $CN^*$  and  $C_2^*$  as function of distance at  $8J.cm^{-2}$  and  $35J.cm^{-2}$ , we remark that their maxima are in the same region and the  $CN^*$  intensity is more important than the  $C_2^*$  intensity for both laser fluence. The maximum intensity occurs at the same distance of 7mm for both  $C_2^*$  and  $CN^*$  transient maximum emission intensity. The  $C_2^*$  and  $CN^*$  emission occur up to distance of 15mm while at  $35J.cm^{-2}$ , the intensity maximum occurs at 5mm and the emission is detectable up to 7.5mm.

From the z-t plot of the transient maximum emission intensity of  $C_2^*$  and  $CN^*$ , at  $8J.cm^{-2}$ , it is found that the speed is the same for both molecules along the observation zone, while, at  $35J.cm^{-2}$ , the  $C_2^*$  molecule appears fast than  $CN^*$  molecule up to 4mm, but the molecules speed are smaller than that obtained at  $8J.cm^{-2}$ .

At  $35J.cm^{-2}$ , the transient emission of  $N_2^+$  molecule is characterised by a prompt emission at the same time the laser reach the target surface, while at  $8J.cm^{-2}$ , this prompt peak is followed by a broad emission with time evolution similar to that of  $N^*$  and  $C^*$ .

The curve of the transient maximum emission intensity of  $N^*$  as function of distance from the target surface present a plateau until 4mm for  $8J.cm^{-2}$  and 7mm for  $35J.cm^{-2}$ , and decrease abruptly beyond these distances.

No emission from neutral atomic nitrogen is seen.

## In-situ Surface Analysis by Laser-Induced Break-Down Spectroscopy

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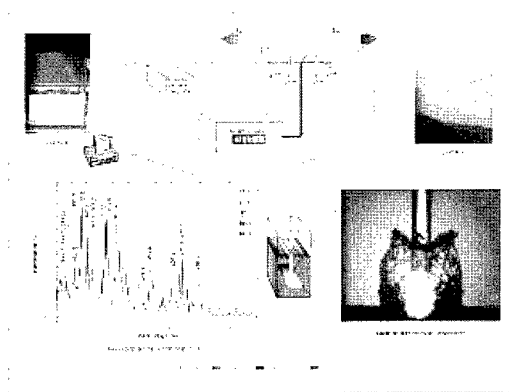
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Pulsed laser radiation of suitable wavelength can be used to ablate any material sample at negligible damage conditions ( $\mu\text{m}$  region), while thus exciting fluorescent light emission. This fluorescence is signatored by it's broad-band plasma-light emission as well as, delayed, by molecular, atomic or even isotope-selective emission spectra. Time or spectrally resolved analysis using an optical multichannel analyser (OMA) allows immediate multiple element proof using a single excitation pulse. Spectroscopic resolution on laser-induced micro-plasma (laser induced breakdown spectroscopy, LIBS) in combination with optical fibers is especially suitable for in-situ analysis at otherwise difficult-to-access sites such as in pipelines or in aggressive environments (Pratisto et al., 1996). In cases of fluid-covered surfaces, however, this method generally fails due to the strong fluorescence quenching of liquids. Our investigations show, however, that the atmospheric-similar contents of a cavitation bubble formed at the tip of a fiber in fluid can still allow optical-analytic spectroscopy to be carried out. Auto-fluorescence of, or a following resonant excitation by a second laser pulse of gaseous ablation products from, the excited probe allows direct results to be obtained. Low pressure in the cavitation bubble during the expansion phase also reduces the quenching process through collision processes and also reduces the fluorescent line width (van Leeuwen, 1993).

Systematic analytic investigation of the ablation process and cavitation bubble dynamic on inorganic materials (e.g. steels, non-ferrous metals, Cu, Ca, In, Si) and organic materials (polymers, biological samples) have been carried out using ultra-fast photography, optical emission spectroscopy and laser-induced fluorescence spectroscopy (Nyga et al., 1991, Tschirner et al., 1993). Using flexible, contact-free, in-site quartz fiber technology, this method allows intensive surface investigations without the need for extraction or preparation of samples as in time- and cost-intensive conventional chemical analysis.

The target of further work is to develop the technique for use in the control of production processes, use in quality control functions and in investigations into corrosive processes in steels also in air and in liquids.



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## Novel Application of Single-Fibre LIBS: Quantitative Analysis of Solids Submerged Under Water

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The analysis of solids submerged under water is a desirable although not an immediately obvious example of how remote LIBS is normally implemented. This is because the delivery and collection of the light to and from the target is rather troublesome. From early tests it became clear that an air environment has to be created on the sample surface for the plasma. This can be done by using a double-pulsed laser ablation technique<sup>1,2</sup>, where the first pulse creates a "bubble", within which the next pulse generates the analytical plasma. While workable, such methods are usually difficult to implement, especially if the water or other liquid becomes opaque to the laser beam and plasma emission, when carrying out the analysis over distances of several meters. Here we propose a novel fibre set-up primarily to determine the identity of solid samples submerged in liquids which does not depend on the state of transparency of the water.

Using a miniature single-fibre analysis probe, incorporated into a gas feed line (ordinary plastic tubing), a quasi-gaseous air environment was created at the ablation area on the target. When the end of the gas feed pipe was presented to the target surface, a dynamic gas cavity is formed within which the plasma can be generated. In order to fit the fibre delivery system down the small diameter gas feed pipe and into a capillary tube nozzle, any distil optics were omitted and the fibre tip was positioned just above the sample surface within the gaseous cavity. By placing the fibre-end close to the sample surface, the energy density is sufficiently high for plasma generation for numerous metallic samples. Also, because of the close proximity of the fibre-end to the sample surface sufficient light is collected for plasma analysis, without the need for a collimating lens.

We demonstrate this easy-to-apply technique for determining (qualitatively) the identity of samples submerged in liquids. The technique is applicable to real-time and in-situ monitoring of difficult-to-reach objects under-water in situations where distil optics can not be used, due to target access limitations put on the probe diameter, e.g. small orifices. Such examples include: the monitoring of steel bars through cracks in under-water bridge constructions; the testing of structural components of oil rigs; and the analysis of sediments in secondary water storage tanks at (nuclear) power stations, to name but a few examples.

With respect to the quantification aspect, calibration graphs typical for LIBS could be generated, and the detection limits and spectral reproducibility achieved with our simple-fibre system without distil optics were not dissimilar to measurements for carefully optimised set-ups. It also should be noted that results using our device did not differ, whether the sample was submerged in a clear liquid, in turbid or dirty water, or simply placed in air. Some representative examples will be discussed.

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## Evaluation of LIPS for Microanalysis and Elemental Mapping in Solids

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As the focalisation of a laser beam results intrinsically in reduced laser-surface interaction, the interest of using Laser Induced Plasma Spectroscopy (LIPS) for microanalysis has been perceived by many authors. Relative to existing techniques currently used in microanalysis, the potential advantages of LIPS lie mainly in the fact that it can be performed directly at atmospheric pressure and both on conducting and non conducting materials. Moreover the simple and robust instrumentation used in optical emission is well adapted to analytical industrial controls. But microanalysis has some specific constraints for which an evaluation of LIPS has to be performed :

- the true lateral resolution, defined as the lateral dimension of the sample surface affected by each measurement, must be well known and controlled in order to be able to attribute the signal to the exact position of the measurement on the sample surface
- quantification is difficult because the sample must be intrinsically considered as "non homogeneous" for the considered lateral resolution, and generally no element is known with a sufficient level of precision to be used as "internal standard"
- sensitivity could be insufficient because reducing the lateral resolution leads to a strong reduction of the probed sample volume

To do this evaluation, a dedicated instrumentation has been developed. It is based on the focalisation of a quadrupled multimode Nd-YAG laser (266 nm) on the sample surface by a Cassegrain type microscope objective. A careful attention has been paid to the homogeneity of the spatial distribution of the beam intensity in the focal plane.

Optimisation of the experimental parameters were performed by measuring the size of the crater formed in different materials by individual laser shots. The results obtained show that exceptionally high laser-surface coupling efficiency can be obtained under the experimental condition of microanalysis. This result in crater depths of few microns for a single laser shot (irradiance around 20 GW/cm<sup>2</sup>). In such conditions, the laser ablation process is few dependent of the sample surface quality, leading to a very good shot to shot reproducibility.

LIBS measurements were performed by coupling the "laser ablation head" to a 500 mm focal length spectrometer equipped with an intensified linear photodiode array. Emission of the plasma was imaged onto the spectrometer entrance slit by the microscope objective used for the laser beam focalisation.

The intrinsic analytical performances obtained in terms of lateral resolution, reproducibility and accuracy will be presented. Quantitative elemental mapping performed on some materials (steel, aluminium, minerals...) will be presented and compared to results obtained with the electron microprobe.

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## Trace Element Measurements and Material Identification using Multivariate Analysis

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The standard procedures in the evaluation of LIBS spectra are univariate analysis methods, normally referencing a spectral peak of the analyte element against a matrix element. However, in general, univariate analysis is imprecise and encounters severe problems if the spectral lines used in the analytical evaluation procedure are close to neighbouring, interfering peaks of other elements. It has been shown that multivariate analysis may offer a solution to the problem of line interference (in the context of LIBS see e.g. Schechter *et al*, 1994). For a number of spectrochemical analysis techniques, e.g. Raman spectroscopy, multivariate algorithms are now routinely incorporated as menu options into industry-standard software packages, such as e.g. GRAMS/32, for spectrum analysis.

We have applied a range of multivariate implementations to qualitative and quantitative LIBS analysis, based on GRAMS/32, and compared the results to standard univariate methods. Ultimately, we selected the most promising approach - the Partial Least Squares (PLS) algorithm. Briefly, PLS deconstructs spectra into weighted factors which represent the most common variations matching the changes in concentration between samples. In particular, PLS can account for analyte peak interferences, and is able to remove noise from the analysis by the exclusion of low-order factors. This results in improved trace concentration measurement precision and accuracy (see Krustev *et al*, 2000). Furthermore, when particular calibration models are used to measure trace concentrations in unknown samples an indication of how well the sample is "matrix-matched" to the calibration samples is given. This allows the analyst to assess the suitability of the calibration for quantitative analysis, and in how far matrix problems, which are frequently reported for LIBS can be accounted for.

This novel analysis approach is exemplified here for the analysis of Si, Co, Nb and P in steel samples; said elements are known to be notoriously difficult to detect due to often extremely low concentrations and to line interference.

Most of the applications for which remote-LIBS is perceived to be commercially suitable involve the identification and sorting of materials, using spectral libraries of the suspect compounds. Comparison to these can be carried out using semi-quantitative univariate analyses which utilise normalised single peak-height measurements. Alternatively, a far superior procedure can be applied which is based on multivariate pattern recognition algorithms. These use the factors and scores determined from the spectral libraries (using Principle Component Analysis (PCA)) to categorise "unknown" spectra. The Discriminant Analysis method demonstrated here for material identification is the *Mahalanobis Distance*. It has been applied to the problem of sorting Al, Cu, Pb, Zn, glass, mild steel and stainless steel (including grade). We have shown that LIBS can be used, in principle, to identify and sort materials with a 100% success rate.

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## ***LIPS++*™: A New Software for Automated Analysis of LIBS Spectra**

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The analysis of LIBS spectra is usually performed with commercial software developed for other spectral techniques or with 'home-made' programs, which are in general instrument-specific and operator-dependent.

The IFAM group has realized *LIPS++*™, a friendly and versatile program that is able to operate automatically on all kinds of LIBS spectra, regardless of the specific experimental set-up and the instruments used for acquiring the spectra themselves.

*LIPS++*™ operates on standard ASCII files, performing a number of operations on the spectra, including:

- Joining and splitting of spectral files
- Wavelength conversion and shifting
- Efficiency correction
- Automatic background subtraction
- Smoothing and interpolation
- Peak finding
- Automatic tagging of peaks with emitting atomic elements
- Multi-peak fitting

Moreover, *LIPS++*™ implements the Calibration-Free algorithm developed by the IFAM group, allowing for automatic, fast and accurate quantitative analysis of spectra. The use of specific templates speeds up the spectral analysis procedure; several spectra can be sequentially analyzed in batch mode.

The *LIPS++*™ software is written in C++ and runs on Pentium-class computers on Windows 9x platform. The structure of the program allows for a quick integration with instrument-specific acquisition packages.

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## **Development of a Flexible, Integrated LIBS System**

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Laser-Induced Breakdown Spectroscopy (LIBS) measurements are routinely performed in engineering and scientific laboratories throughout the world. However, to date, researchers and practitioners of LIBS have generally assembled their own laser and optical systems, and typically have devised unique software solutions to acquire and process LIBS spectra. This paper reports on the design and development of a flexible, integrated LIBS system coupled with dedicated LIBS software. The hardware includes a Nd:YAG laser capable of roughly 400 mJ pulse energies and repetition rates up to 20 Hz, and an echelle spectrometer with a range of 200-700 nm. The dedicated LIBS software is designed to accommodate a variety of calibration and quantification strategies, to operate in continuous sampling or in a software-filtered sampling mode, and allows database storage and retrieval of spectra.

We will discuss the system heritage, the general features of the system design, and potential applications of the system, with particular emphasis on analysis of particle-laden gas flows and environmental applications.

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## Design, Optimisation and Commercial Application of a LIBS Simultaneous Elemental Analysis System

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A new instrumentation variation on laser induced breakdown spectroscopy (LIBS) is presented that allows simultaneous determination of all detectable elements using a multiple spectrograph and multiple CCD spectral acquisition system. The device has been designed to reduce the cost penalties often associated with the application of LIBS while allowing accurate and precise determination of the elemental composition of bulk materials. The system is particularly suited to the analysis of heterogeneous materials such as coal and mineral ores.

In coal analysis detectable elements include the key inorganic components of coal – such as Al, Si, Mg, Ca, Fe, Na, and K - in addition to C and H. Detection limits vary depending on the particular element, but are typically of the order of 0.01% for as-received, moist materials. *Beta*-versions of the device have been produced and are currently being used routinely in two commercial lignite-fired power stations. The application of these instruments will progressively replace wet chemical methods in this industry. The principal benefit in using the LIBS based instrumentation is the rapid sample analysis time of 30 seconds compared to several hours using conventional analysis procedures. Calibration of the devices has been achieved by the preparation of blended lignite samples covering the range of composition of material that is typically mined.

The design of an effective data analysis methodology has been critical in achieving both accurate and reproducible results from the technology. Using gypsum as the optimisation matrix, various data analysis techniques have been investigated including pulse-to-pulse normalisation, software filtering, spectra deconvolution and partial least squares chemometric analysis. A combination of spectral deconvolution and pulse-to-pulse normalisation has been found to yield the best results. For many elements the typical uncertainty in the analysis has been reduced to  $< \pm 10\%$  which compares favourably to analysis by conventional techniques for these materials. Furthermore, the use of pulse-to-pulse normalisation extends the instrument recalibration period to once per month, thus enhancing the ease of use of the device.

## Transportable, Multi-purpose, Commercial LIF-LIBS System

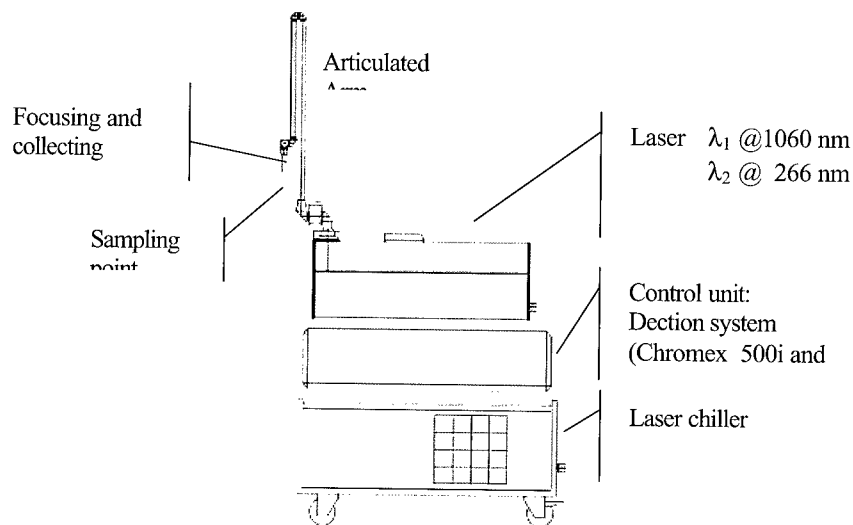
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*SOING S.r.l.*

A transportable LIP-LIBS system has been developed. The Laser Induced Brakdown Spectroscopy (LIBS) and the Laser Induced Fluorescence (LIF) techniques are combined into a single system. The system uses a Quanta System Nd-YAG laser, with 300 mJ per pulse at 1064nm and 80 mJ at 266nm. The laser beam is delivered by a seven mirrors articulated arm with, at the end, a focusing fused silica focusing optics to produce the plasma. The emitted plasma light is collected by a fused silica objective with an aperture of 5 cm and focused into an optical fiber bundle of 100 fibers of 100µm of core. The optical fiber is interfaced to a polychromator model Chromex 500i compled to an Andor ICCD camera. In the LIBS configuration a 2400 gg/mm holographic grating is used. The system is easily turned into the LIF configuration by the activation of th 4<sup>h</sup> armonic generator wich deliver up to 80 mJ per pulse @266 nm and selecting in the Chromex the 150 gg/mm ruled grating . The fluorescence signal in acquired by the same optical system used for the LIBS. The whole system is controlled by a PC integrated within the appartaus. A specific, user friendly, software has benn developed for both spectra acquisition and analysis.



The combination of the two techniques offers a wide range of application.

Up to now the system has been succesfully tested as environmental diagnostic tool a fast for qualitative and quantitative analysis of heavy metal in soil (LIBS) and for the detection of Hydrocarbons contamination in soil (LIF). Field sensitivity up to 1- 10 ppm is reached.

In the LIBS configuration good results were also obtained in alloys characterization.

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## A Fully-Automated Instrument for Stainless Steel Composition Surveillance Using Laser-Induced Breakdown Spectrometry

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Stainless steel manufacturers must provide customers with a quality certificate stating the chemical composition and a reference code in connection with the heat number, among other parameters. However, identification errors inducing to mixing-up may occur during processes further to the heat, such as cold or hot rolling. In order to overcome such problems a sample has to be cut from the final rolled product at the delivery time and sent to the laboratory where it is prepared for X-ray fluorescence analysis and then compared to the composition of the corresponding heat sample. This is a time-consuming procedure lasting no less than 5 minutes.

In the present work, the development of a fast alternative using laser-induced breakdown spectrometry (LIBS) is presented. An instrument capable to decrease the assessment time in stainless steel process to 35 seconds has been built and evaluated. A laser-to-fiber robust interface has been developed which permits safe and reliable transmission of the laser beam without gradual degradation of the fiber optic. As an additional benefit, laser beam at the output of the fiber optics presents an homogeneous transverse profile which produces very flat craters. Based on a depth profile study of stainless steel components on samples with variable surface finish, reproducible analytical results are obtained. Enhanced off-axis light collection results in better signal-to-background ratios without significant signal drift. Multivariate calibration for elemental analysis with LIBS has revealed as a valuable tool for the correction of matrix effects and spectral interferences in certain cases. Assessment by comparison of the analysis results was accomplished with a 100% of success in the tests carried out with real samples.



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## On-Site Scrap Classification for Stainless Steel Production Using a Portable Laser Analyzer

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One of the major inconveniences found in stainless steel production is the classification of scrap. A rapid chemical characterization is essential on the reception time in order not only to assess the value of a shipment, but also to proceed with its adequate classification. Loading a electric arc furnace is a delicate operation mainly guided by a final steel-composition target. Although the composition of the first molten can be corrected by the addition of binary alloys (Fe and Cr, Ni, Ti or Mo), the use of such materials is not cost-effective. Consequently, the overall composition of the scrap entering the furnace must be as close as possible to the final composition required.

The analytical needs of the problem entail on-site classification of the samples into main stainless steel grades according to the sample content of Cr, Ni, Ti and Mo. The scrap is received at the factory in pieces of highly variable size and shape. Also corrosion, grease and dust maybe present at the surface. Traditionally, such issues have been overcome to some extent by visual examination with experienced personnel and by choosing random samples for analysis in the factory laboratory. Therefore, owing to the lack of accuracy and the time needed by such solutions, the study of new approaches seems more than reasonable.

The present work describes the development of a portable laser spectrometer as a feasible response to the analytical problem. The system integrates a 50 mJ per pulse Nd:YAG laser operating at 1064 nm, a 1/8 m spectrometer, a CCD detector and a PC computer for the coordination of the whole instrument operation and interfacing with user. A fiber optic is used to guide the laser light to the sampling probe where it is focused into the sample to form a plasma whose emission is collected using the same optical arrangement. Major instrument features are operated from two buttons placed in the sampling probe. Its design is intended to provide sampling stability and easy handling. Analysis results are shown in a LCD screen and stored in the instrument database.

Results obtained both in the lab and in the field will be discussed regarding the analytical precision, the capability to distinguish between scrap grades and the difficulties observed with sample variability.

## **Development of a Method for the Automated Quantitative Analysis of Ores Using LIBS**

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In an effort to increase the energy and cost efficiency of mineral exploration and extraction, the US Department of Energy in conjunction with the US National Mining Association is sponsoring a project to develop LIBS methods for the real-time analysis and grading of ore at the mine site during the extraction process. This paper reports the development of a method for the real-time automated quantitative analysis of mineral ores using a commercial LIBS instrument, TRACER™ 2100, fitted with a recently developed computer controlled auto-sampler. The auto-sampler permits the execution of methods for performing calibrations and/or analysis of multiple elements on multiple samples. Furthermore the analysis is averaged over multiple locations on each sample, thus compensating for their heterogeneous morphology. The results for Phosphate ore are reported here, but similar methods are being developed for a broad range of ores and minerals.

The supplied known composition Phosphate ore samples used for calibration contained the minerals  $P_2O_5$ , CaO, MgO, SiO and  $Al_2O_3$ . A method was developed and programmed that automatically performed calibrations for the elements P, Ca, Mg, Al and Ca. The spectral line for each desired element was selected with respect to the best combination of peak intensity and minimum interferences from other lines. This is a key step, because of the observed matrix dependence of LIBS-OES analysis. The optimum combination of the time interval between the laser firing (plasma formation) and signal detection and the duration of this optical detection was then determined for each element. These parameters were found to have a significant effect on spectral line intensity and resolution.

Utilizing the developed method, it was found that the instrument was capable of analyzing the required elements in the phosphate ore samples supplied, with a very good level of precision and accuracy. Calibrations were achieved for P, Ca, Mg, Al and Si with  $R^2$ 's of 0.97, 0.99, 0.98, 0.97, and 0.98, respectively. Precision on individual samples and from sample to sample were typically in the range of 2-3% relative standard deviations (RSD) of 2-3 % for most elements analyzed. The time for preparation and analysis of each sample was less than five minutes.

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## **Recent Advances in Laser-Induced Breakdown Spectroscopy for Industrial Applications**

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The advanced steel industry is faced with the challenge of producing higher quality, higher purity and cleaner steel, while at the same time increased productivity has to be achieved through costs savings and additional production. LIBS presents large potentialities to meet these requirements and the first commercial instrument based on this technique, the ARL Laser Spark, was launched in 1998.

Blast furnace materials are ideal candidates for LIBS since both conductive (pig irons) and non conductive (slags) samples have to be analyzed. Moreover, both types of samples may be analyzed straight from the blast furnace, without preparation, whereas usual analysis by X-ray fluorescence requires special sample conditioning. Several ARL Laser Spark are now in operation at blast furnaces in France, Belgium and Italy.

In this context we will present key features of the instrument and its performances in blast furnace applications.

Furthermore, new prospects for the use of LIBS in industrial environment are now clearly identified, such as: on-line inclusion and segregation analysis, quantitative analysis of pieces with lateral dimensions less than 1 mm, and depth-resolved analysis. Along those lines, the promising outlook of LIBS, shored up by preliminary results, will also be addressed .

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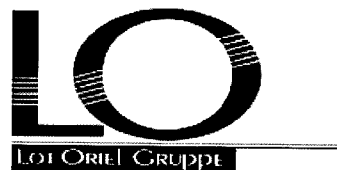
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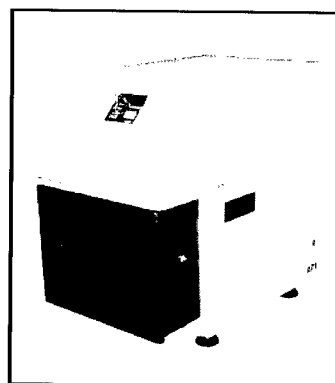


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an instrument for comfortable routine or on-line  
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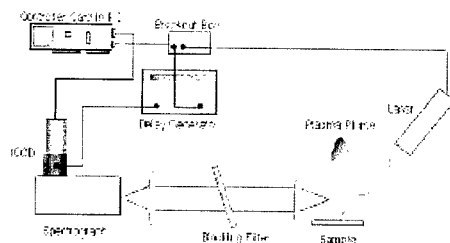
- No sample preparation
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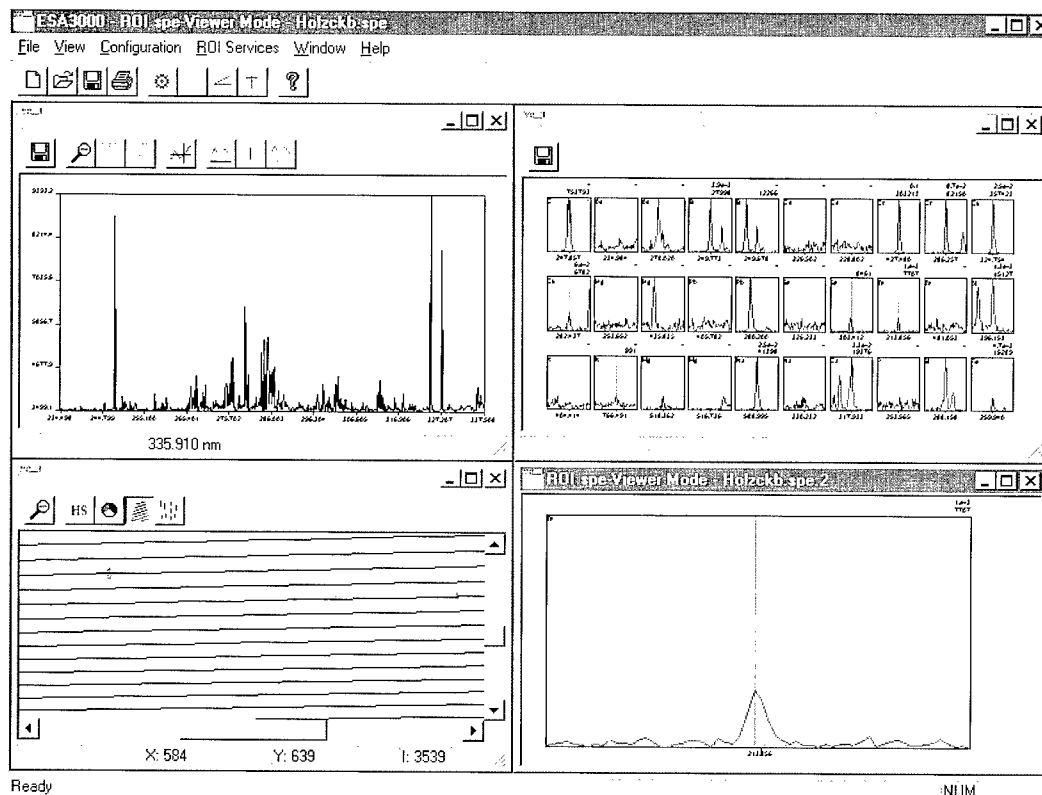
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# Ultra Fast Multi-Element-Analysis

## The Tasks:

- Control of Products and Processes
- Qualitative and Quantitative Analysis
- Simultaneous Real-Time Measurement of almost all Elements
- Without Sample Preparation and without Protective Gas



## The Solutions:

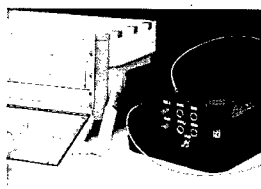
### LIPAN 3001

- Compact laser plasma analyzer
- All components built in mobile measuring system



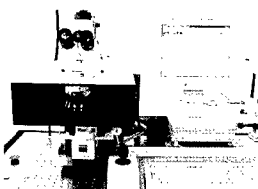
### ESA 3000

- Echelle Spectra Analyzer
- Wavelength: 200 - 780 nm
- Resolution ( $\lambda/\Delta\lambda$ ) with respect to one pixel: 40000



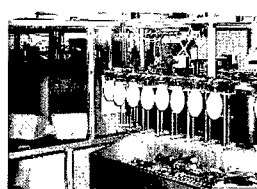
### LIPAN 3010

- Microscope module with a laser-spectrometer system
- Visualisation of sample region by additional camera



### LIPAN 3002

- Components separated for on-line applications
- Modular system for user-defined requirements



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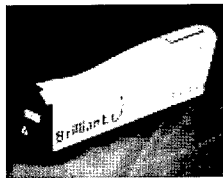


LLA Umwelttechnische Analytik und Anlagen GmbH

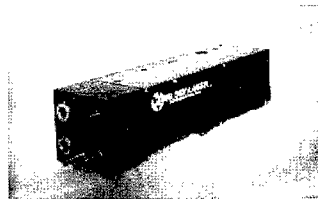


Backed up by a 30 years experience in the field of solid-state pulsed Nd:YAG lasers, the name of Quantel has come to mean reliability and innovation throughout the world. Quantel's unique know-how has enabled it to develop the original and innovating "BRILLIANT" concept, and a complete range of associated products:

**BRILLIANT, BRILLIANT B & CFR Series**  
(compact oscillators) and their harmonic generators, ...



*Brilliant & Brilliant B head*



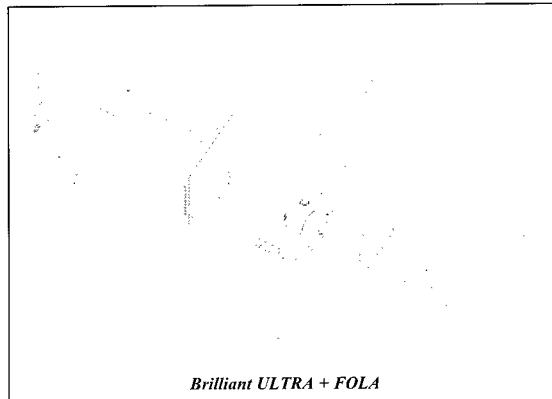
*CFR200/400 head*

They can be equipped with harmonic generators emitting visible or ultraviolet light. The standard product is designed to be insensitive to the external environment (e.g. industrial environment) and can be installed and serviced with no special training. The lasers are used for Laser Cleaning, **LIBS**, **LIF** and **PIV**.

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Several systems are implanted in industrial environments and research laboratories all over the world.

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*Brilliant ULTRA + FOLA*

- A single compact Head delivering 50 mJ at 1064 nm (20 Hz)
- A compact fibre injection with a 1 mm fibre and  $\geq 40$  mJ output power

Quantel provides a complete series of compact, robust and sealed **single oscillator Nd:YAG** laser systems with different energies in the IR and at its different harmonics:

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- These systems provide average powers up to 40W at repetition rates from 10 Hz to 120 Hz.

**The Quantel Group**

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web : [www.quantel.fr](http://www.quantel.fr)

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finito di stampare  
nel mese di Ottobre 2000



	Sun 8 Oct.	Mon 9 Oct.	Tue 10 Oct.	Wed 11 Oct.	Thu 12 Oct.
08:30-09:00		Opening Ceremony			
09:00-09:40		Oremers	Anglos	Cheung	Round Table on LIBS perspective
09:40-10:00		Margetic	Sodo	Pershin	
10:00-10:20		Sabsabi	Cefalas	St. Onge	
10:20-10:40		Tognoni	Burgio	Haisch	
10:40-11:10		Coffee Break			
11:10-11:50		Mizielek	Hermann	Schachter	Round Table on LIBS perspectives
11:50-12:10		Morel	Telle	Tabares	
12:10-12:30		Samek	Hilbk	Mateo	
12:30-12:50		Bechard	Tarasenko	Hemmerlin	Closing Ceremony
13:00-14:30		Lunch			
14:30-15:10		Noll	Smith	Aguilera	
15:10-15:30		Green	Hahn	Branci	
15:30-15:50	Uhl	Adam	Gornushkin		
15:50-16:10	Panne	Yoshie	Ee-D Gamal		
16:10-16:30	Deguchi	Whitehouse	Colonna		
16:30-17:00	Coffee Break				
17:00-17:20	Welcome Cocktail	Alexander	Liebermann	Shakatov	
17:20-17:40		Vidal	Fichet	Apostol	
17:40-18:00		Hergenroder	Caceres	Cabalin	
18:00-19:30		Poster Session		Excursion	
21:30-23:00		Italian Opera Concert	Neapolitan Music Concert		
23:00-01:00					

	Mon 9 Oct	Tue 10 Oct	Wed 11 Oct	Thu 12 Oct
09:00-10:40	Session 1:  Fundamentals of LIBS	Session 5:  LIBS for Cultural Heritage	Session 9:  New LIBS Methodologies	Round Table on LIBS perspectives (I)
10:40-11:10	Coffee Break			
11:10-12:50	Session 2:  LIBS in Life science	Session 6:  Hyphenated techniques	Session 10:  Imaging, Surface Mapping & Stratigraphy by LIBS	Round Table on LIBS perspectives (II)  Closing ceremony
12:50-14:30	Lunch			
14:30-16:30	Session 3:  LIBS for material analysis	Session 7:  LIBS for Environment (I)	Session 11:  Modelling of Laser Induced Plasmas	
16:30-17:00	Coffee Break			
17:00-18:00	Session 4:  Femtoseconds LIBS	Session 8:  LIBS for Environment (II)	Session 12:  Laser Ablation and deposition	